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[*Authors alone are responsible for all opinions expressed in their Communications.*]

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No. 18

ON A RECENT ADDITION TO THE COLLECTION OF IRISH METEORITES IN THE NATIONAL MUSEUM DUBLIN.

By

H. J. Seymour, B.Sc., B.A., M.R.I.A.
(Professor of Geology, University College, Dublin.)

[Read November 26, 1946. Published separately May 15, 1947].

(Plate 12.)

Since the year 1795 falls of meteorites represented by museum specimens have numbered only sixteen in these Western Islands. Seven of the falls occurred in England, five in Ireland, three in Scotland, and one, the latest in date (April 14th 1931), at Pontlyfni, Carnarvonshire, in Wales. A phenomenon of this nature is sufficiently uncommon to attract considerable attention at the time of its occurrence, but not infrequently some of the fragments recovered are lost or mislaid subsequently, especially if they pass into private hands.

Such fortunately was not the ultimate fate of the present meteorite, the largest individual fragment yet known to have fallen in Ireland, or indeed in Great Britain, viz. one of the component parts of the ' Limerick ' meteoritic shower of September 10th, 1813. All the stones of this particular fall were dispersed over an area lying between Faha House (north of Patrickswell) and Adare, some three miles distant to the south-west. There were recovered ultimately three large and some six or seven smaller pieces, the weights of the former being recorded as about 65, 24, and 17 lbs. respectively. It was known that the 17 lb. specimen is in the Oxford University museum, and that the smaller stones are in various British, Irish, and Continental museums, but the whereabouts of the two larger ones was not hitherto known in scientific circles. This is still true of the 24 lb. specimen, but the largest one, commonly referred to as the ' *Brasky* ' mass, has again come to light and is the subject of the present paper. Though it fell in 1813, no detailed description of it has hitherto been published, only the approximate weight and shape being noted in the more or less contemporaneous accounts of the incident.

Its re-discovery is due to Mr. J. A. Morrison of the Irish Land Commission, who late in November 1945 in the course of a routine inspection of a recently allocated holding near Rathkeal, Co. Limerick, noticed in the house of a small farmer, Mr. John Collins of Hollypark, Kilkornan, Co. Limerick, a large stony mass which he

recognised as of extra-terrestrial origin. He advised the owner to have it examined at the National Museum, at the same time notifying Dr. O'Connor, the Acting Director, of its location. On communicating with Mr. Collins, the latter readily consented to forward it to the Museum, where I made a superficial examination, and pointed out the desirability of its purchase for our mineral gallery. This was ultimately arranged to the satisfaction of the parties concerned, and this fine meteorite became museum property. Before the negotiations had been concluded, Mr. Collins gave permission for the removal of a small chip for micro and chemical examination, and I had a section prepared which was later seen and compared with sections of the same fall in the British Museum, by Dr. Hey. In a letter to me he states :—

> " We have compared it with our specimens and we are satisfied that there is no visible difference and that the mass can certainly be accepted as authentic. It is a veined grey chondrite agreeing in all particulars with the description of the Limerick mass quoted in Prior's catalogue (3), and the fragments and sections agree perfectly."

There is therefore little doubt but that our recent find is an integral portion of the meteoritic shower of 1813.

The tradition in the Collins family is that the ' thunderbolt ' remained in the possession of the Tuthills of Faha House, whose then owner recovered it from his lands following its observed fall. Later it passed into the custody of the Taylors of Hollypark (near Askeaton) on intermarriage with the Tuthills. When their estate was purchased some seven or eight years ago from its owner, Miss C. E. Taylor, an auction was held at which the meteorite was acquired by Mr. Collins. According to the latter it was not put up separately but included in a miscellaneous lot and

> " no one took any particular interest in it and I thought it of no earthly value, other than its having a sentimental one for me, since our family had worked for generations for the Tuthill and Taylor families, and my father (now aged 85) was also glad to have the stone as a souvenir."

Mr. John Collins stated further that it was his own grandfather who over seventy years ago, actually brought this meteorite, with other articles of furniture, etc. from Faha House to the home of the Taylors at Hollypark. It would appear therefore that this particular specimen has been what may be described as " under observation " by some member of the Collins family for much more than eighty years, if not indeed for the whole period since its finding in 1813.

Discrepancies in the weights recorded for meteorites are of common occurrence, so that the fact that our specimen weighs some five and three quarter pounds less than the reputed weight of the Brasky mass, does not necessarily imply that it is a separate entity. This alternative would be most unlikely, since such a large mass could not possibly be preserved and yet remain unknown to the local magnates in a typical rural area. It is much more probable that the originally recorded weight was incorrect by reason of the methods or apparatus used.

The first account of the Limerick episode appeared in the local newspaper, the Limerick Chronicle of Sept. 11th 1813 as follows—

"Yesterday morning about nine o'clock, there was the most dreadful thunder heard in the direction of from Patrickswell towards Adare and Askeaton, in this county; the peals were very violent, continued for some time and were accompanied with some awful appearances, large fragments of atmospheric stones, and other circumstances, which indicated some very serious concussion to have taken place."

The earliest account, in a scientific publication, appeared in the Phisophical Magazine of 1818 (2), five years after the event, in the form of a communication to its Editor from William Higgins, Professor of Chemistry to the Dublin Society, now the Royal Dublin Society. It was accompanied by a copy of a letter forwarded to Higgins by one Samuel Maxwell of Limerick, and containing information about the fall of 1813 supplied by Mr. George Tuthill, near whose home (Faha House) the meteoritic shower occurred. This is the communication commonly referred to as Maxwell's letter though in fact it is Tuthill's.

For our purpose the relevant data contained therein are as follows :—

"One (meteorite) fell on the lands of Scagh in the neighbourhood of Patrickswell and was immediately dug up, being warm and weighing 17 lbs. about. Six or seven similar but smaller stones descended between the lands of Scagh and the village of Adare.

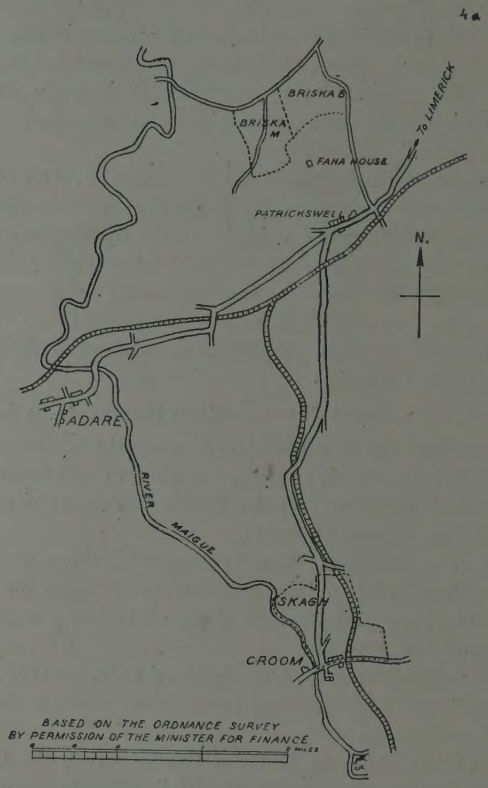
One more very large mass came to ground on the lands of Brasky, buried itself to a depth of two feet, and was not dug up for two days, it was fractured in places and weighed about sixty-five pounds. Its shape was rather round but irregular.

At the same time there fell on the lands of Faha another stone unfractured, of irregular shape and weighing twenty-four pounds, which is now in my (Tuthill's) possession.

It is three miles from the lands of Brasky where the large stone fell, to the village of Adare, where the small stones were picked up, and all the others fell intermediately."

Another account of the same event appears in a brief footnote on page 430 of Linehan's 'Limerick and its Antiquities' published in the year 1866, and therein it is mentioned that one of the stones is in the possession of Mr. Tuthill, and weighs four stones weight. It may be assumed from the foregoing that the two largest fragments at least were once in the possession of Mr. Tuthill, and that the special reference to the 24 lb. specimen in his own account above, was due to its being unfractured, thus differing from the 65 lb. mass.

An examination of the Ordnance six-inch maps show that the Faha demesne on which the 24 lb. fragment fell, is bounded on the north and north-west by the two townlands of Briska More and Briska Beg. Locally Briska is pronounced as if spelled Brisky, and this is clearly the 'Brasky' area of Maxwell's letter. The precise situation of the 'lands of Scagh' is not readily determinable. There is a townland of Skagh some five miles to the south near the village of Croom, but this cannot be regarded as being 'in the neighbourhood of Patrickswell' nor does it occupy an intermediate position between Brasky and Adare, stated to have been the terminal points of the track of the Limerick meteoritic shower of 1813.



The relative positions of the places named here are shown on the accompanying map based on the 1″ Ordnance sheets, 143 and 153. From all the evidence available it seems probable that locally in the past, the term 'lands of Scagh' indicated the general area of the two Briska townlands and further, that all the larger fragments fell in the vicinity of Faha House and demesne. In this connection it may be noted that the account in Maxwell's communication suggested a direction of travel for the stones from east to west. Generally since smaller objects encounter more resistance relatively to their mass than do the larger ones in any meteoritic shower, the former should reach the ground at nearer points and at a steeper angles, whereas the latter owing to their greater momentum will normally carry further in the direction of travel. The known distribution of the fragments of this shower would therefore suggest a motion from west to east, or actually south-west to north-east.

The general form is well shown in the accompanying photographs (Plate 12), which also indicate the essentially irregular characteristics of a typical rock fragment. Roughly speaking its shape is that of an irregular three-faced truncated double

pyramid, the overall dimensions being about 32 x 26 x 21 cm., or say 12½ x 10 x 8½ inches. About two-thirds of the specimen lies above the level of its greatest width, and one-third below (Fig. 1). There are numerous faces of varying sizes, some slightly concave and others convex, and mostly glazed all over with a thin brownish black skin of fused-rock material. The faces vary in type, the larger number being deeply ' thumb-marked ' and slightly concave (Figs. 1 and 2). About one-third of the total surface area consists of relatively smooth and slightly convex faces, probably of later origin, but with a well fused crust on which incipient ' thumb, marks ' are rather sparsely distributed (Fig. 3). Another type of face constituting the larger proportion of the residual surface, shows only partial or incipient glazing in the form of flow ridges or flashings of fused material, in some places more conspicuously developed than in others. (Fig. 2). These illustrate a stage preliminary to the formation of an all over surface crust, and in the present case clearly belong to a late period of the meteorite's travels through our atmosphere. At the base and elsewhere small fracture surfaces, without any obvious glaze, occur, and are referable to some form of impact, and to the same cause may be due the two prominent fissure planes which show up on the base. (Fig. 4).

In its present state the meteorite weighs 27,060 grams, or say fifty-nine pounds, four and one quarter ounces. The weight of the chip removed prior to this weighing was 42 grams, and from this a thin section was made and material for chemical analysis supplied. Two small pieces remain weighing together a little over 19 grams.

The density as determined from this chip was found to be 3.84, that of a fragment from Adare in the Trinity College, Dublin, collection was 3.64. A specimen analysed by Apjohn (1) in 1874, is recorded as having a density of 3.94, from which it would appear that the distribution of the nickel-iron content in the meteorite is irregular.

This meteorite belongs to the group known as aerolites, which consist essentially of stony matter, of a basic mineral nature, with a low nickel-iron content. Usually their constituents occur as ' chondrules ' or rounded aggregates of the minerals present, in which case the aerolites are classed as ' chondrites.' The latter are again sub-divided according to the percentage of nickel in the nickel-iron present, notice being also taken of structure, colour and mineral composition. Our meteorite is accordingly classed as a *veined grey bronzite-chondrite.*

Under the microscope the section reveals the presence of numerous chondrules, varying in diameters between 0.3 and 1.2 mm., and fairly evenly dispersed in a crystalline matrix, in which there is a good deal of nickel-iron and scarce troilite. (Fig. 5). The small and well rounded chondrules consist mostly of olivine crystals, while the larger and less well rounded ones are composed of aggregates of elongated crystals of bronzite, associated with a small amount of olivine and dark interstitial matter In one or two of the smaller chondrules and elsewhere in the section some colourless material suggests the presence of felspars having a lower refractive index than Canada balsam.

An analysis of one of the Adare fragments of the Limerick fall has been published by Prior (5,) and from it he deduces the mineral composition as follows :—

		%
Felspar	(Na, K, Ca.)	7·53
Chromite		0·87
Apatite	(Merrillite ?)	0·63
Bronzite	(MgO/FeO = 5)	33·83
Olivine	(MgO/FeO = 4)	32·64
Nickel-iron	(Fe/Ni =11)	18·46
Troilite	(FeS)	5·60
		99·56

A partial analysis of the magnetically attracted portion only, of the powder got by grinding down a fragment of the meteorite, was also made according to a method which the same author devised and published in 1919 (4). A portion of the recent find was analysed for comparison, by the same method in our State Laboratory, and both results are recorded below.

	Prior	State Laboratory
	%	%
Insoluble silicate (i) ...	22·35	9·10
Soluble silicate	16·64	4·39
FeS (t)	1·93	0·60
Ni (n)	4·93	7·23
Fe (+ Co) by difference ...	(54·15)	(78·68)
P	—	traces not estimated
	100·00	100·00
Weight of Attracted ...	2·7384 g.	2·636 g.
,, ,, Unattracted ...	6·1524 ,,	10·493 ,,
Percentage of Nickel-iron	18	17·26
Ratio of Fe (+ Co) to Ni	11	10·88
Group.	C_2	C_2

It will be observed that there are concordant results in both analyses in respect of the nickel-iron content and also for the iron-nickel ratio. A separate analysis to determine the Fe + Co content of the attracted portion of our meteorite gave 78·50%, which corresponds with that got by ' difference '. The variation in the silicate content is due to the fact that Prior's aim was primarily to obtain a metal-free silicate residue. In our case the endeavour was essentially to obtain a metallic residue free from silicate. The method of separation by magnets in any event depends on so many varying factors that concordant results cannot be expected in all cases.

The following is a list of the British and Irish meteoritic falls, represented by museum specimens, which have been recorded since 1795. The arrangement is geographical, and only the weight and present location of the largest and heaviest fragment now extant are recorded below for each individual fall.

England.	*Date of fall.*	*Wt. in grams.*	*Repository.*
Wold Cottage, Yorkshire ...	13/12/1795	20,638	British Museum
Launton, Oxfordshire ...	15/2/1830	998	,, ,,

Aldsworth, Gloucestershire ...	4/8/1835	520	,, ,,
Rowton, Shropshire ...	20/4/1876	3,109	,, ,,
Middlesborough, Yorkshire ...	14/3/1881	1,546	York Museum.
Appley Bridge, Wigan, Lancs.	13/10/1914	10,900	British Museum.
Ashdon, Essex	9/3/1923	1,270	,, ,,
Ireland.			
Moorsfort, Tipperary ...	—/8/1810	1,208	National Museum, Dublin.
Adare, Limerick	10/9/1813	27,060	,,
Killeter, Tyrone	29/4/1844	90	British Museum.
Dundrum, Tipperary ...	12/8/1865	1,638	Trinity College, Dublin.
Crumlin, Antrim	13/9/1902	3,821	British Museum.
Scotland.			
High Possil, Glasgow ...	5/4/1804	91	British Museum.
Perth, Perthshire	17/5/1830	1½	,, ,,
Strathmore, Perthshire ...	3/12/1917	9,911	Royal Scottish Museum, Edinburgh.
Wales.			
Pontlyfni, Carnarvonshire ...	14/4/1931	142	Private.

In conclusion the writer desires to express his personal indebtedness to Dr. Hey of the British Museum and Dr. Spiller of the Oxford University Museum for their kind assistance and interest. He wishes also to thank Dr. O'Connor for giving him the privilege of describing this historic meteorite, and for his ready co-operation in the negotiations leading up to its purchase. Thanks are specially due to Mr. J. A. Morrison of the Irish Land Commission, who is primarily responsible for the re-discovery of the Meteorite, and also to Mr. J. A. Collins, who, if his means had permitted, would have been willing to present it to the National Museum once its scientific interest had been brought to his notice. Messrs. Avery of Middle Abbey Street, Dublin, were good enough to furnish facilities for the accurate weighing of this heavy specimen, and Mr. K. O'Kelly and Mr. D. Ryan prepared the map reproduced here.

Models are being prepared in the workshops of the Museum for ultimate distribution to selected institutions and overseas museums as well as to Mr. John Collins its previous owner.

The photographs (1, 2 and 3) on Plate 12 are so arranged that they represent successive faces of the specimen on rotation in an anti-clockwise direction, about an axis coincident with the direction of maximum length of the meteoritic.

Explanation of Plate 12.

Fig. 1. The face here consists of two slightly concave surfaces separated by a low sinuous ridge, each section showing characteristic ' thumb-marks.' The dominant bi-pyramidal form is noticeable. Maximum dimensions 32 x 25 cm.

Fig. 2. A smaller face also ' thumb-marked ' and nearly flat. On the left are fracture surfaces almost entirely in the third stage of development but some are of still later origin. One of the former is conspicuous on the N.W. margin, showing darker in colour, with distinct parallel fused or flow ridges running N.E. and S.W. Maximum dimensions 32 x 22 cm. (excluding part of face 1 on right below).

Fig. 3. The widest face of the meteorite, well glazed, rather smooth, and slightly convex, showing comparatively few ill-developed ' thumb-marks.' One of the two fracture planes can be traced on the right. A small thumb-marked face occurs below. This is the only aspect of the meteorite that approximates to Tuthill's description as " round but irregular." Maximum dimensions 32 x 27 cm.

Fig. 4. Base of meteorite (the face at right angles to direction of maximum elongation which is vertical in Figs. 1, 2 and 3) showing on the more recent fracture surfaces the character of the grey crystalline matrix. Most of these surfaces show a flash of incipient glazing. One completely fused face, like that predominating in Fig. 3, occurs on the right, while above, portions of the thumb-marked (1 and 2) faces are seen. The two intersecting fracture planes may also be traced in the photograph. Maximum dimensions 28 x 22 cm.

Fig. 5. Micro section (x 10) showing chondrules. Most of the dark material is nickel-iron. The dark more-or-less rectangular crystal below the large round chondrule is troilite, and portion of a typical olivine chondrule occurs near it. The oval-shaped chondrule at top of section consist mainly of bronzite crystals.

References.

(1) *R. Apjohn.* Chem. Soc. Jour. **12.** p. 104. 1874.
(2) *W. Higgins.* Phil. Mag. **51.** p. 355. 1818.
(3) *G. T. Prior.* Catalogue of Minerals in the British Museum, p. 99. 1923.
(4) ————————Mineralogical Magazine. **18.** p. 352. 1919.
(5) „ „ **19.** p. 169. 1921.

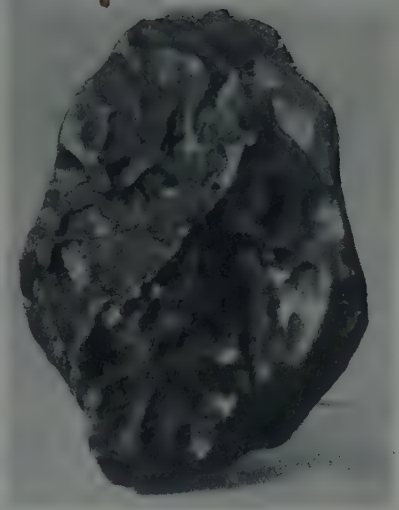


Fig. 1

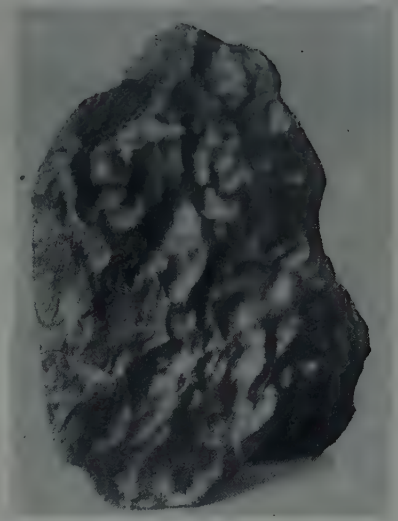


Fig. 2

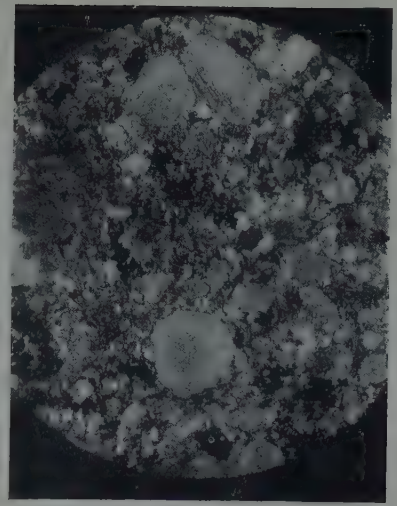


Fig. 5

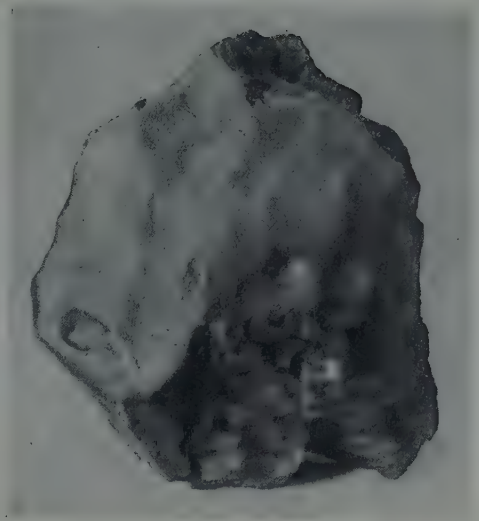


Fig. 3

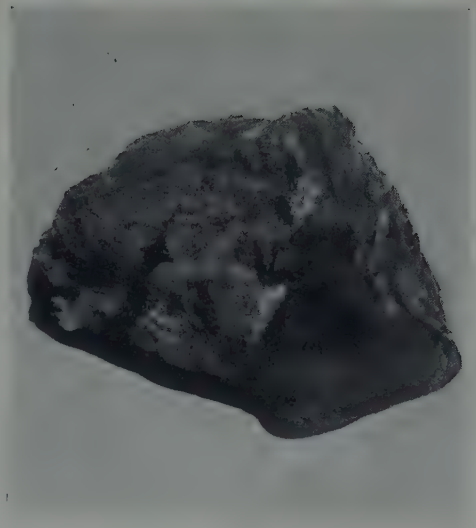


Fig. 4

No. 19.

IRISH SALMON, 1945.

By

ARTHUR E. J. WENT,

(Department of Agriculture, Fisheries Branch, Dublin.)

[Read November 26, 1946. Published separately May 17, 1947.]

In a preliminary investigation made in the year 1944 (Went, 1945) the proportion of previously spawned fish in a number of Irish rivers was determined. On that occasion the material consisted of a single scale taken from just below the dorsal fin from about 25,000 salmon captured in some twenty five Irish rivers. Such material was satisfactory for the purpose for which it was intended, but in 1945 it was decided to modify the method of collection, and the collectors were asked to scrape off a few scales from the region just below the dorsal fin in the case of as many fish as possible, and to preserve the scales from each individual fish in separate envelopes, specially provided for the purpose. The scales from each month were to be kept separate. In this way it was hoped to obtain some information additional to that available in the previous year.

Over 8,300 sets of scales were obtained from 25 localities, eight rivers furnishing inadequate material consisting of less than 100 sets of scales. A list of the rivers investigated, together with the names of the persons collecting the material, has been given in Table 1 (see Appendix for all tables). The writer wishes to take this opportunity of thanking the collectors, without whose collaboration this investigation would have been impossible.

Methods.

A typical scale selected from each sample was cleaned in dilute sodium peroxide solution, and was mounted with the aid of dilute gelatine solution on a microscope slide. Subsequently the scales were examined under the microscope, and the details of the life history of the individual fish ascertained.

Smolt Ages.

The fish were divided into four smolt classes, namely the one-, two-, three-, and four-year smolts (see Table 2). In every river the bulk of the fish belonged to the two-year smolt class, and, save in the case of the Waterville, Sligo, and Erne

Rivers, the one-year smolts were more important than the three-year smolts. Only two four-year smolts were observed in the present material, showing clearly that this smolt class is unimportant in Irish salmon.

One might now ask how the present results compare with the previous investigations on some of the rivers investigated in 1945. In Table 3 the present results were compared with the results obtained in previous investigations. In general, the order of the values obtained is the same, the only noticeable exception being that of the Corrib in which in 1945 the proportion of three-year smolts showed some diminution. Even in this case the results are such as might be expected in a normal river from year to year.

Smolt Types.

In previous investigations on Irish salmon (Went, 1938–1946) it was mentioned that some fish showed marked growth in fresh water in the spring immediately prior to migration as a smolt, whereas other fish showed no such growth. Those fish showing marked growth were, for convenience, designated type B smolts, and those in which growth was limited to two new growth elements or less were designated type A smolts. In the present material the division into the two types in the various smolt classes has been made and the results are given in Table 4.

The two-year type B smolts formed the bulk of the fish in every river investigated in 1945. A similar condition was also observed in most of the previous investigations on Irish salmon, the only notable exception being the Ballisodare River (see Table 5).

Age Groups.

The distribution of the different age groups (as percentages of the total catch) in the various rivers investigated have been indicated in Table 6. Local and other inquiries have shown, however, that in 1945, apart from the poor runs of fish generally, grilse were scarce. This was particularly noticeable in the case of the Rivers Boyne, Waterville and Lee. In addition the large spring fish, have for some years, decreased considerably in numbers in many rivers throughout Ireland.

Whilst the present results do not afford an exact indication of the proportion of the various age groups, owing to the unavoidable fluctuations in the proportion of fish sampled throughout the season, the results do give a fairly clear idea of the runs of fish into the rivers in question. It seems probable also that the figures given in the last line of Table 6 represent, to some degree, the conditions prevailing in Ireland generally in 1945. Certainly the grilse (1 + winters) and the small spring fish (2 winters) are the most important age groups, followed by the small summer fish (2 + winters) and either the large spring fish (3 winters) or the previous spawners (with SMs). The large summer fish (3 + winters) and the very large spring fish (4 winters) are unimportant in the stocks of salmon in the country as a whole. They are, in fact, to be found in very few rivers throughout the country.

A comparison of the present results with those of previous investigations as regards the distribution of the various age groups is given in Table 7. The only comment necessary in this connection is that the proportions of grilse (1 + winters)

in the 1945 runs were less than in previous years, additional proof, if such was necessary, of the previous statement that these fish were scarce in 1945 in most Irish rivers. A later section will be devoted to consideration of the previously spawned fish.

DISTRIBUTION OF THE YEAR CLASSES (BROOD OF A PARTICULAR YEAR).

In Table 8 the distribution of the fish in the various rivers into the appropriate year classes has been given. No general condition can be followed in the various rivers except that the bulk of the fish in all the rivers were spread over not more than two year classes. There was, in fact, almost a complete gradation from the state existing in the Corrib and Moy, where the two most important year classes were approximately of the same strength, to the Kerry Blackwater, where nearly 90% of the fish were derived from the one year class. Taking the country as a whole four-year-old fish (i.e. the 1941 year class) were more important than three-year-old fish (i.e. the 1942 year class).

A comparison of the present results with those of previous investigations has been made, Table 9. The more important differences exhibited in this respect can be attributed in the main to the reduced runs and catches of grilse in 1945.

THE PREVIOUS SPAWNERS.

In a previous paper (Went, 1945) dealing with Irish previously spawned salmon it was clear that there was a great variation in the proportion of previously spawned fish in the different rivers. In 1944 the variation was from 0.6% in the River Liffey to 9.5%in the River Erne. During the present investigation an even greater variation was found (see Table below) namely from 0.6% in the River Boyne to 15.4% in the River Erne.

River	Percentage of previous spawners in 1945	Percentage of previous spawners in 1944
Boyne	0·6	1·2
Lee	1·0	1·2
Liffey	2·3	0·6
Ballisodare	2·9	2·4
Cork Blackwater	3·2	2·5
Feale	3·9	1·8
Kerry Blackwater	4·0	5·1
Sligo	4·8	4·5
Laune	5·4	3·3
Shannon	5·7	4·1
Bandon	5·9	8·3
Waterville	7·3	5·8
Moy	8·2	4·3
Corrib	11·2	7·5
Bundrowes	11·4	7·3
Erne	15·4	9·5
Total for all rivers combined	5·4	4·3

In general, the proportion of previously spawned fish was higher in 1945 than in 1944. It is also noteworthy that in rivers in which the proportion of previously spawned fish was very low in 1944 (Rivers Liffey, Lee, and Boyne) it was also low in 1945. Similarly where in 1944 the proportion of previous spawners was very high (Rivers Bundrowes, Corrib, and Erne) it was also very high in 1945. It is unfortunate that sufficient material was not available from the Ilen, which in 1944 showed a high proportion of previous spawners. With the exception of the Bandon River, all the rivers having more than the average proportion of previous spawners had on the river system one or more large lakes through which salmon had to pass to reach the sea. On the other hand in cases where the proportion was low there were no large lakes frequented by salmon on the river. The Ballisodare River has a sizeable lake (Lough Arrow) on one of its tributaries, but salmon do not run into the lake. The very high proportions for the Moy, Corrib, Bundrowes, and Erne in 1945 can be attributed partly to the exceedingly poor runs of grilse. With the exception of the Bundrowes, the other three rivers rely for the most part on grilse, which were very scarce in 1945 throughout most rivers in Ireland.

In all, the scales of 460 fish having spawning marks thereon examined, 428 (93%) had one spawning mark, 30 (6·5%) had two spawning marks, and 2 (0·5%) had three spawning marks. The two fish from the River Erne having three spawning marks were the first of this type to be observed in investigations on salmon from Irish rivers. Previous spawners can be classified on (*a*) the length of sea life before the first spawning, and (*b*) the absence habit or the period spent feeding between what would have been, but for the intervention of capture, two successive spawnings. In Table 10 the fish have been so classified. Excluding those fish which one could identify merely as having been previous spawners, there were 425 fish the " absence habit " of which could be determined. Of these 211 (49.7%) exhibited the short absence habit (less than a full year), 197 (46.3%) exhibited the long absence habit (a full year), 16 (3.8%) exhibited the very long absence habit (more than a full year) and one appeared to have been two years feeding in the sea between its descent as a kelt and reappearance as a clean fish. As regards the age at first spawning, there was a tendency for the proportion of fish to decrease as the age groups are ascended. For example, fish which first spawned as grilse comprised 61.1% of all previous spawners, those spawning first after two years sea life 34.6% and so on. It seems probable that the smaller fish tend to survive to a much greater extent after spawning than the larger fish.

RÉSUMÉ.

1. Collections of scales were made in a number of Irish rivers during the salmon season of 1945.

2. Scales representing 8,300 fish from twenty-five Irish rivers were mounted and examined microscopically.

3. Two-year-old smolts were most important in all rivers examined (Tables 2 and 3), and the one-year-olds were more important than the three-year-olds in all rivers except the Waterville, Sligo, and Erne Rivers.

4. Two-year type B smolts formed the most important smolt type in every river examined (Tables 4 and 5).

5. The age groups in which the fish have spent less than three full years feeding in the sea together formed over three-quarters of the total in every river. (Tables 6 and 7). Grilse were scarcer in 1945 than usual, as were also the large spring fish.

6. In most rivers two year-classes (i.e. the brood of two years) accounted for the bulk of the fish. There was, however, a gradation from the condition found in the Kerry Blackwater where one year-class accounted for 88·5% of the fish to the conditions found in the Corrib and Moy where the two most important year classes were almost of equal strength. (Tables 8 and 9).

7. The proportion of previous spawners ranged from 0·6% (Boyne) to 15·4% (Erne), the average for all rivers being 5·4% which is somewhat higher than in 1944. The order of the rivers arranged in 1945 (see Table page 167) was similar to that for 1944. Of the fish having spawning marks on their scales 93% had one spawning mark, 6·5% two spawning marks, and 0·5% three spawning marks. The absence habit and age at first spawning was indicated (Table 10).

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Appendix.

Table I. Sources of material and collectors. The rivers are arranged clockwise from Dublin.

River	Name of Collector
Liffey	Mrs. ffrench Davis
Blackwater (Cork)	Mr. G. Fitzgerald
Lee	Mr. J. Scanlon
Bandon	Mr. W. J. Seymour
Ilen	Mr. R. Beamish
Sheen	Mr. W. Johnstone
Blackwater (Kerry)	Colonel E. Hood
Waterville	Mr. J. Butler
Laune	Mr. A. de C. Dodd
Feale	Mr. G. Gleasure
Shannon	Mr. L. Forde
Corrib	Lt. Col. E. G. K. Cross, D.S.O.
Newport	Mr. M. Kelly
Owenduff, Owenmore, Carrowmore Lake	Mr. P. J. Lenehan
Moy	Mr. W. P. Stevens
Ballisodare	Mr. F. F. Scott
Sligo	Mr. W. T. Middleton
Bundrowes	Mr. J. Cassidy
Erne	Mr. T. Mac D. Swan
Owenea	Mr. F. A. Watson
Lennon	Sir J. Stewart
Crana	Miss H. Moore
Boyne	Capt. R. Law Mr. P. J. Tiernan

Table 2. Distribution of the various smolt ages as percentages of total number of fish examined (maiden fish only).

River	Smolt Age			
	1 year	2 years	3 years	4 years
Liffey	15·2	80·5	4·3	—
Blackwater (Cork)	14·7	83·7	1·6	—
Lee	17·8	81·2	1·0	—
Bandon	18·9	76·5	1·0	—
Blackwater (Kerry)	2·7	95·4	1·9	—
Waterville	3·2	90.3	6·5	—
Laune	5·4	92·4	2·2	—
Feale	2·6	96·8	0·6	—
Shannon*	12·8	81·0	6·2	—
Corrib	17·4	76.1	6·3	0.2
Moy	15·4	80·0	4·6	—
Ballisodare	14·4	82·4	3·2	—
Sligo	5·5	87·3	7·2	—
Bundrowes	10·7	84·9	4·4	—
Erne	4·8	88·6	6·6	—
Boyne	19·3	76·6	4·0	0.1
All rivers combined	11·9	84·1	4·0	+

* Weighted figures from Went (unpublished data).
+ =trace (less than 0·05%.)

Table 3. Comparison of present results with those of previous investigations as regards the distribution of the various smolt ages. (As percentages).

River	Year or years investigated	Reference	Smolt Ages			
			1 year	2 years	3 years	4 years
Liffey	1933–35	Frost and Went, 1940	12·2	85·4	2·4	—
	1940–41	Went, 1946	16·6	80·5	2·9	—
	1945	Present results	**15·2**	**80·5**	**4·3**	—
Kerry Blackwater	1943	Unpublished data	1·3	97·4	1·3	—
	1945	Present results	**2·7**	**95·4**	**1·9**	—
Waterville ...	1941	Went and Barker, 1943	5·1	86·0	8·9	—
	1945	Present results	**3·2**	**90·3**	**6·5**	—
Shannon* ...	1941	Went, 1943	11·5	83·3	5·0	0·2
	1944	Unpublished data	8·2	78·9	12·9	—
	1945	Present results	**12·8**	**81·0**	**6·2**	—
Corrib	1924–26	Went, 1943	11·8	75·2	12·5	0·5
	1945	Present results	**17·4**	**76·1**	**6·3**	**0·2**
Ballisodare ...	1938	Went, 1941	22·9	75·2	1·9	—
	1939	Went, 1941	18·8	80·3	0·9	—
	1945	Present results	**14·4**	**82·4**	**3·2**	—
Erne	1928	Went, 1942	4·8	92·0	3·2	—
	1945	Present results	**4·8**	**88·6**	**6·6**	—

* Results given only relate to this river since the advent of the hydro-electric scheme.

Table 4. Percentage of each smolt type in each smolt class in maiden fish only in the different rivers.

Smolt Age		All rivers combined	Liffey	Cork Blackwater	Lée	Bandon	Kerry Blackwater	Waterville	Laune	Feale	Shannon	Corrib	Moy	Ballisodare	Sligo	Bundrowes	Erne	Boyne
Type A	2	13·8	20·3	20·5	19·8	17·1	11·7	13·8	8·2	12·9	5·8	6·8	17·7	16·2	6·2	12·6	5·6	24·3
	3	2·3	2·3	—	1·0	1·0	0·5	4·0	1·3	0·6	2·1	3·5	3·9	2·2	4·2	2·2	2·1	3·2
	4	+	—	—	—	—	—	—	—	—	—	0·2	—	—	—	—	—	0·1
	Total	16·1	22·6	20·5	20·8	18·1	12·2	17·8	9·5	13·5	7·9	10·5	21·6	18·4	10·4	14·8	7·7	27·6
Type B	1	11·9	15·2	14·7	17·8	18·9	2·7	3·2	5·3	2·6	12·8	17·4	15·4	14·4	5·5	10·7	4·8	19·3
	2	70·3	60·2	63·2	61·4	63·0	83·7	76·5	84·2	83·9	75·2	69·3	62·3	66·2	81·1	72·3	83·0	2·3
	3	1·7	2·0	1·6	—	—	1·4	2·5	0·9	—	4·1	2·8	0·7	1·0	3·0	2·2	4·5	0·8
	Total	83·9	77·4	79·5	79·2	81·9	87·8	82·2	90·5	86·5	92·1	89·5	78·4	81·6	89·6	85·2	92·3	72·4
Mean age in years*		2·03	1·92	1·96	1·92	1·93	2·10	2·13	2·09	2·09	2·05	2·01	2·00	1·99	2·13	2·04	2·12	1·94

* On assumption that the type B growth = $\frac{1}{8}$ year. + = trace (less than 0·05%).

Table 5. Comparison of present results with those of previous investigations as regards the distribution of the various smolt types in the various smolt classes. (As percentages).

Rivers	Year or Years investigated	Reference	Smolt types						
			A			B			
			Smolt class (years)			Smolt class (years)			
			2	3	4	1	2	3	4
Liffey ...	1933–35	Frost and Went, 1940	24·4	2·4	—	12·2	61·0	—	—
	1940–41	Went, 1946	15·3	1·3	—	16·6	65·2	1·6	—
	1945	Present results	**20·3**	**2·3**	—	**15·2**	**60·2**	**2·0**	—
Kerry Blackwater	1943	Unpublished data	13·2	1·3	—	1·3	84·2	—	—
	1945	Present results	**11·7**	**0·5**	—	**2·7**	**83·7**	**1·4**	—
Waterville	1941	Went and Barker 1943	13·4	5·0	—	5·1	72·6	3·9	—
	1945	Present results	**13·8**	**4·0**	—	**3·2**	**76·5**	**2·5**	—
Shannon* ...	1941	Went, 1943	14·7	3·5	0·2	11·5	68·6	1·5	—
	1944	Unpublished data	10·2	9·6	—	8·2	68·7	3·3	—
	1945	Present results	**5·8**	**2·1**	—	**12·8**	**75·2**	**4·1**	—
Corrib ...	1924–26	Went, 1943	14·6	8·6	0·4	11·8	60·6	3·9	0·1
	1945	Present results	**6·8**	**3·5**	**0·2**	**17·4**	**69·3**	**2·8**	—
Ballisodare	1938	Went, 1941	32·7	0·8	—	22·9	42·5	1·1	—
	1939	,, ,,	41·6	0·6	—	18·8	38·7	0·3	—
	1945	Present results	**16·2**	**2·2**	—	**14·4**	**66·2**	**1·0**	—
Erne ...	1928	Went, 1942	15·1	2·9	—	4·8	76·9	0·3	—
	1945	Present results	**5·6**	**2·1**	—	**4·8**	**83·0**	**4·5**	—

* Results given only relate to the river since the advent of the hydro-electric scheme.

Table 6. Distribution of the different age groups (as percentages of the total catch in the various rivers.

River	Age group (in winters)						
	1+	2	2+	3	3+	4	With SMS.
Liffey	12·2	47·0	16·0	22·1	—	0·4	2·3
Cork Blackwater ...	6·4	64·2	19·8	4·8	—	1·6	3·2
Lee	3·8	90·0	3·4	1·8	—	—	1·0
Bandon	34·8	36·5	18·6	3·4	0·8	—	5·9
Kerry Blackwater ...	90·3	1·7	4·0	—	—	—	4·9
Waterville	6·0	81·7	3·3	1·7	—	—	7·3
Laune	37·4	48·1	8·1	1·0	—	—	5·4
Feale	26·8	62·5	6·5	0·3	—	—	3·9
Shannon	65·8	19·4	7·0	2·1	—	—	5·7
Corrib	41·5	31·1	15·8	0·4	—	—	11·2
Moy	36·0	35·0	20·5	0·3	—	—	8·2
Ballisodare	72·9	15·9	8·2	0·1	—	—	2·9
Sligo	1·1	92·1	1·3	0·7	—	—	4·8
Bundrowes	37·1	45·4	5·0	0·8	0·3	—	11·4
Erne	50·2	7·1	25·2	1·7	0·2	0·2	15·4
Boyne	1·7	45·2	37·7	14·1	0·4	0·3	0·6
All rivers combined ...	33·9	42·6	14·3	3·7	0·1	0·1	5·4

Table 7. Comparison of present results with those of previous investigations as regards the distribution of the various age groups. (As percentages).

River	Year or years investigated	Reference	Age group (in winters)						
			1+	2	2+	3	3+	4	With SMS.
Liffey ...	1940–41	Went, 1946	14·7	49·0	13·1	20·8	0·1	—	2·3
	1945	Present results	**12·2**	**47·0**	**16·0**	**22·1**	—	**0·4**	**2·3**
Kerry Blackwater	1943	Unpublished data	86·7	4·2	6·7	—	—	—	2·4
	1945	Present results	**90·3**	**1·7**	**4·0**	—	—	—	**4·0**
Waterville	1941	Went and Barker, 1943	32·9	55·4	2·5	2·0	—	—	7·2
	1945	Present results	**6·0**	**81·7**	**3·3**	**1·7**	—	—	**7·3**
Shannon* ...	1941	Went, 1943	75·0	9·0	9·6	0·7	—	0·1	5·6
	1944	Unpublished data	74·2	15·6	4·6	2·1	0·1	—	3·4
	1945	Present results	**65·8**	**19·4**	**7·0**	**2·1**	—	—	**5·7**
Corrib ...	1924–26	Went, 1943	61·4	16·6	14·7	0·9	0·4	—	6·0
	1945	Present results	**41·5**	**31·1**	**15·8**	**0·4**	—	—	**11·2**
Ballisodare	1938	Went, 1941	81·3	6·3	6·0	—	—	—	6·4
	1939	,, ,,	82·6	6·3	5·4	0·2	—	—	5·5
	1945	Present results	**72·9**	**15·9**	**8·2**	**0·1**	—	—	**2·9**
Erne ...	1928	Went, 1942	58·7	7·5	25·2	1·7	0·5	—	6·4
	1945	Present results	**50·2**	**7·1**	**25·2**	**1·7**	**0·2**	**0·2**	**15·4**

* Results given only relate to the river since the advent of the hydro-electric scheme.

Table 8. Years in which fish were hatched (as percentages of the total for the year).

River	Years in which fish were hatched							
	1936	1937	1938	1939	1940	1941	1942	1943
Liffey ...	—	—	—	3·4	21·0	52·7	22·1	0·8
Lee ...	—	—	—	1·0	1·0	77·0	20·5	0·5
Bandon ...	—	—	—	2·5	5·9	42·4	45·8	3·4
Kerry Blackwater ...	—	—	—	—	0·1	9·9	88·5	1·5
Waterville ...	—	0·4	—	3·3	8·0	80·0	8·3	—
Laune ...	—	—	0·2	2·5	3·7	52·8	38·9	1·9
Feale ...	—	—	—	2·3	1·3	67·7	28·1	0·6
Shannon ...	—	—	—	1·6	2·5	28·4	60·9	6·6
Corrib ...	—	—	—	2·1	4·2	43·8	45·8	3·9
Moy ...	—	—	0·2	3·6	4·3	45·5	43·8	2·6
Ballisodare ...	—	—	—	0·6	2·4	20·9	66·8	9·3
Sligo ...	—	—	—	0·2	12·1	81·3	5·3	1·1
Bundrowes ...	—	—	—	7·5	5·0	46·0	38·2	3·3
Erne ...	0·4	—	—	4·8	5·2	41·7	46·5	1·4
Boyne ...	—	—	—	0·7	12·9	71·3	15·1	—
All rivers combined ...	+	+	+	2·1	5·7	49·8	39·8	2·6

+ = trace (less than 0·05%).

Table 9. Comparison of present results with those of previous investigations as regards the distribution of the various " year groups " of salmon. (As percentages of the total catch).

River	Year or years investigated	Reference	Year group*							
			9	8	7	6	5	4	3	2
Liffey ...	1940–41	Went, 1946	—	—	0·2	2·6	17·4	55·5	22·3	2·0
	1945	Present results	—	—	—	**3·4**	**21·0**	**52·7**	**22·1**	**0·8**
Kerry Blackwater	1943	Unpublished data	—	—	—	0·3	0·6	14·0	85·1	—
	1945	Present results	—	—	—	—	**0·1**	**9·9**	**88·5**	**1·5**
Waterville ...	1941	Went and Barker, 1943	—	—	0·3	4·3	7·7	54·4	32·2	1·1
	1945	Present results	—	—	—	**3·3**	**8·0**	**80·0**	**8·3**	—
Shannon†	1941	Went, 1943	—	—	0·4	1·3	3·6	19·3	67·8	7·6
	1944	Unpublished data	—	—	0·1	0·6	2·8	31·3	60·6	4·6
	1945	Present results	—	—	—	**1·6**	**2·5**	**28·4**	**60·9**	**6·6**
Corrib ...	1924–26	Went, 1943	—	—	0·2	1·4	7·1	30·6	56·4	4·3
	1945	Present results	—	—	—	**2·1**	**4·2**	**43·8**	**45·8**	**3·9**
Ballisodare ...	1938	Went, 1941	—	—	—	2·1	0·8	9·5	72·4	15·2
	1939		—	—	—	0·2	1·3	9·6	76·4	12·7
	1945	Present results	—	—	—	**0·6**	**2·4**	**20·9**	**66·8**	**9·3**
Erne ...	1928	Went, 1942	—	—	0·1	4·2	4·3	32·6	57·6	1·2
	1945	Present results	**0·4**	—	—	**4·8**	**5·2**	**41·7**	**46·5**	**1·4**

* Length of river and sea life combined.
† Only observations since inception of hydro-electric scheme included.

Table 10. Absence habit and age at first spawning in the previous spawners.

Absence habit	Age at first spawning (in winters)				
	1+	2	2+	3	Total†
Short (less than a full year)	190	—	8	—	211(49·7%)†
Long (a full year) ...	—	111	—	3	197(46·3%)†
Very long (more than a full year) ...	8	—	3	—	16 (3.8%)†
Total ...	198 (61·1%)	112*(34·6%)	11 (3·4%)	3 (0·9%)	425†*

† Including fish of which the age at first spawning could not be determined.
* Includes one S.M.2 fish mentioned in test.

No. 20.

SALMON OF THE KERRY BLACKWATER.

By

ARTHUR E. J. WENT.

(Read November 26, 1946. Published separately May 21, 1947).

Friar O'Sullivan of Muckross Abbey in his *Ancient History of the Kingdom of Kerry* describes this river in the following terms. " The river Blackwater, the bounds 'twixt the parish of Templenoe and Ballybogg, noted for pearls and the salmon fishing in the Summer season, but deserves further notice that ye salmon goes on it two or three miles and within musket shot to the source thereof called Loch Brin, having in their way of said miles many cataracts and falls till coming to a smooth ford that has neither, which they never pass, nobody able to discover the secret . . ." (*Cork Hist. Soc. Jn.* 2nd Ser. 6, 149).

Cosmopolite in his book *The Sportsman in Ireland* (1840, 1, 130) refers to this river and states " The strictness with which this river has been preserved has rendered

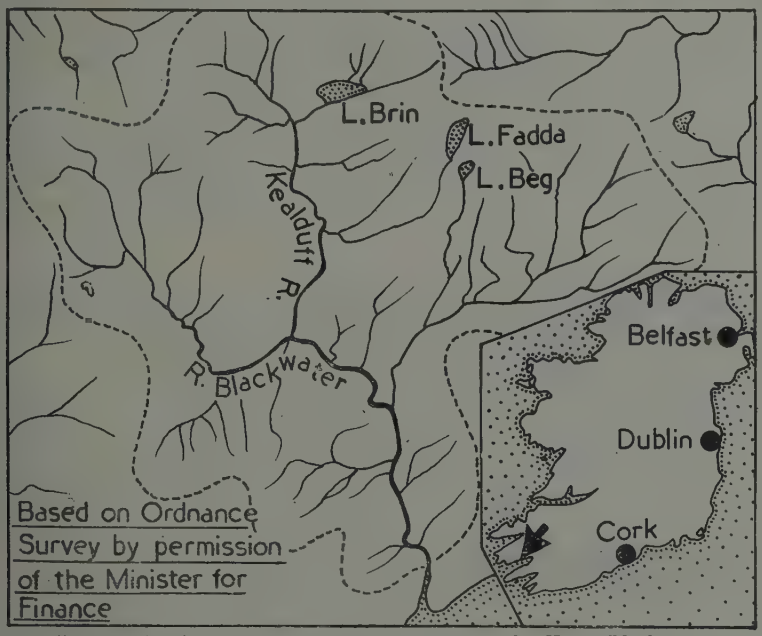

Fig. 1. Sketch map of the catchment area of the Kerry Blackwater (Arrow in inset map indicates location of the Kerry Blackwater).

nearly all the scattered inhabitants adepts in the art of fly-fishing." *The Parliamentary Gazetteer of Ireland* (1846, 1, 260) also describes the river picturesquely " It trots, tumbles and leaps noisily along a rugged path, at the bottom of a deep, copse-clad steep-sided ravine ; and a little above its embouchure, rushes headlong beneath an aerially-poised bridge of two arches, spanning its yawning chasm. The stream has nearly as high attractions for the angler as for the poetic lover of landscape."

The Kerry Blackwater is a very small river with a catchment area of only 34 square miles and a length of approximately 10 miles. It drains some relatively high ground, some over 2,000 feet above sea level, and in consequence is a spate river. It has a number of small lakes on its watercourse and that of its tributaries, the most important of which is Lough Brin (see Fig. 1). The rocks of the catchment area belong mainly to the Old Red Sandstone, and therefore the waters thereof tend to be acid in character. There are adequate spawning grounds available, and it is noteworthy that the annual yield to the nets alone per square mile of the catchment area over the period 1875–1945, both years inclusive, has amounted to 43 salmon and peal, or about 300 lb. weight. Yields up to 105 salmon and peal per annum to the nets alone per square mile of catchment area, or about 740 lb. have been recorded. The Kerry Blackwater is a prolific river which affords first class angling when water conditions are satisfactory from the month of June onwards.

Material.

In 1943 a small collection of sets of scales and measurements (83 in number) of salmon and grilse (peal) taken in the nets in the estuary was made. In 1944 material was collected for the determination of the proportion of previously spawned fish in that river (see Went, 1945) and in 1945 further material, consisting solely of 595 sets of scales (without measurements), was collected from the fish taken by nets in the estuary. The possibility of obtaining more suitable material was remote, and therefore it was thought well to place the results of this limited examination on record.

Smolt Ages.

Three smolt classes, one, two, and three years, were observed in the maiden fish. The bulk of the fish belonged to the two-year smolt class (see Table 1).

Smolt Types.

In previous publications on Irish salmon (Went, 1938–1946) it was mentioned that there were some fish which showed two or more annuli, corresponding to growth in the spring prior to the smolt migration. These were termed type B smolts. On the other hand there were fish which showed no such growth on their scales. For convenience these fish were termed type A smolts. In the present material the division has been carried out, and the results are given in Table 2.

Age Groups.

In both 1943 and 1945 the fish were divided into three groups of maiden or unspawned fish and one heterogeneous group of previously spawned fish, having only one common character, namely the presence of spawning marks on their scales.

There were some fluctuations in the proportion of fish sampled throughout the season in 1943, so that the results were weighted against the catch figures. In 1945, however, sampling appeared to be adequate and representative, since the proportion of grilse calculated from the examination of scales was 90.3%, and that estimated from the visual examination of the fish was 89·3%. The weighted figures for 1945 have, however, been given in the various tables.

The grilse formed about nine-tenths of the total catch in both 1943 and 1945. None of the remaining age groups exceeded 7·0% of the total catch by numbers (see Table 3). In April a few summer fish ran into the river, and thereafter they predominated (see Table 4). In 1945 the bulk of the small spring fish ran before the end of May, as did almost half of the small summer fish. The greatest runs of grilse and previously spawned fish occurred in June (see Table 5). No information under this heading could be obtained directly for the year 1943 but all evidence available suggests that a similar condition prevailed during that year. Previously spawned fish comprised 2.4% of the total catch in 1943, 5·1% in 1944 (see Went, 1945) and 4·0% in 1945, respectively.

In Table 6 the years in which the various fish were hatched have been indicated. As should be obvious from Tables 1 and 3 one year class (i.e. the brood of one year) forms almost nine-tenths of the total catch. This fishery depends, therefore, on the spawning season 3½ years earlier, i.e. in 1945 on the spawning season of 1941–42. If this was the only factor operating in determining the abundance of salmon in this fishery one would expect to find a good season followed by other good seasons at regular intervals. Similarly poor seasons should follow one another at the same interval, but such is not the case as will be seen later.

Size Distribution.

The size distribution, as based on the limited material from 1943, has been given in Table 7. It will be seen that just over 70% of the total catch had lengths between 23.95 and 27·95 inches.

Average Sizes.

The average sizes in 1943 in the different age groups have been given in Table 8. It must be acknowledged that the material is very limited, but the results so indicated do not call for any comment. It is obvious that the Kerry Blackwater is a small fish river. Col. E. Hood informs me that a fish of 33 lb. weight was taken about 15 years ago on the rod, and about 6 years ago one of 29 lb. was taken in the nets, but these were exceptional fish. Most of the fish, in fact, are under 10 lb. in weight.

Condition Co-efficient.

The method of determining the condition co-efficient (or condition factor) has been given in an earlier paper (Went, 1941), and the mean values in the various age groups in 1943 are given in Table 9. With an average value of 1·14 on Menzies Scale the condition of these fish is good, being similar to that of salmon of other Irish rivers (see Went, 1938–1946).

Table 1. Distribution of the various smolt ages.

Smolt Age	1943		1945		Combined Results	
	No.	%	No.	%	No.	%
1	1	1.3	16	2.7	17	2.6
2	74	97.4	544	95.4	618	95.5
3	1	1.3	11	1.9	12	1.9
Total	76	100.0	571	100.0	647	100.0

Table 2. Distribution of the various smolt types.

Smolt Age	Smolt type				Both types	
	A		B			
	No.	%	No.	%	No.	%
	1943					
1	-		1	1.3	1	1.3
2	10	13.2	64	84.2	74	97.4
3	1	1.3	-	-	1	1.3
Total	11	14.5	65	85.5	76	100.0
	1945					
1	-	-	16	2.7	16	2.7
2	66	11.7	478	83.7	544	95.4
3	3	0.5	8	1.4	11	1.9
Total	69	12.2	502	87.2	571	100.0

Table 3. Distribution of the various age groups (as percentage of the total catch).

Age Group (in winters)	1943	1945
1+	86.7%	89.2%
2	4.2%	2.1%
2+	6.7%	4.7%
With S.Ms.	2.4%	4.0%

Table 4. Proportion of spring and summer fish in the 1943 and 1945 seasons.

Month	1943		1945	
	Proportion of		Proportion of	
	Spring Fish	Summer Fish	Spring Fish	Summer Fish
April	75.0%	25.0%	-	-
May	42.8%	57.2%	33.3%	66.7%
June	6.3%	93.7%	0.9%	99.1%
July	Nil	100.0%	Nil	100.0%
August	Nil	100.0%	-	-
Whole Season	5.1%	94.9%	1.7%	98.3%

Table 5. The proportion of each age group in each month (as percentage of total catch) in 1945.

Month	Age group (in winters)				Total
	1+	2	2+	With S.Ms.	
April/May	0.8	76.2	49.0	5.0	4.8
June	59.5	23.8	44.6	52.5	57.8
July	39.7	-	6.4	42.5	37.4
Total	100.0	100.0	100.0	100.0	100.0

Table 6. Divided migration and return (as percentage total catch). Note:- These figures have not been weighted against catch figures.

Returned in 1945 as	Hatched in				Total
	1940	1941	1942	1943	
1 winters	-	1.7	87.3	1.5	90.3
2 winters	-	1.2	0.5	-	1.7
2 winters	0.1	3.2	0.7	-	4.0
With S.Ms.	-	3.8	0.2	-	4.0
Total	0.1	9.9	88.5	1.5	100.0

Table 7. Size distribution as percentage of total catch.

Class Interval*	Age Group (in winters)				Total
	1+	2	2+	With S.Ms.	
18	2.0	-	-	-	2.0
20	4.0	-	-	-	4.0
22	7.9	-	-	-	7.9
24	49.6	0.1	-	-	49.7
26	21.7	0.2	-	-	21.9
28	4.0	0.9	0.7	0.7	6.3
30	-	0.5	2.7	-	3.2
32	-	0.2	1.0	2.0	3.2
34	-	0.2	0.3	1.3	1.8
Total	89.2	2.1	4.7	4.0	100.0

* Class interval 18 etc. includes all fish having lengths between 17.95 and 19.95 inches etc.

Table 8. Mean, minimum and maximum weights and lengths in the various age groups.

Age Group (in winters)	Length in inches			Weight in lb.		
	Mean	Min.	Max.	Mean	Min.	Max
1+	25.2	19.5	28.1	6.6	2.0	10.0
2	29.7	25.5	32.3	10.9	6.5	15.0
2+	31.3	28.0	34.5	12 6	9 0	16.5
With S.Ms.	32.7	28.5	35.0	15 0	12.0	18.0
Total	-	19.5	35.0	-	2.0	18.0

Table 9. The mean condition coefficients and condition factors in the various age groups in 1945.

Age Group (in winters)	Mean condition coefficient (K) $K = \frac{W}{L^3 \times 0.00036}$	Mean condition factor (C.F.) $C.F. = \frac{W}{L^3}$
1+	1.14	41.2
2	1.15	41.5
2+	1.14	41.2
With S.Ms.	1.19	43.1
Total	1.14	41.2

W = Weight L = Length

Table 10. Fluctuations in the catches in the Kerry Blackwater and Ballisodare Rivers and the export figures (as percentages of the mean values for the period 1924 to 1945, both years inclusive)

Year	Percentages of mean for the period 1924 to 1945		
	Kerry Blackwater	Ballisodare River	Exports in cwt. June/October from Eire
1924	25	90	124
1925	119	99	122
1926	86	93	143
1927	75	63	117
1928	55	46	79
1929	9	41	54
1930	89	124	109
1931	180	138	128
1932	107	105	120
1933	112	105	93
1934	134	123	156
1935	83	122	114
1936	116	97	92
1937	50	80	42
1938	39	57	44
1939	120	110	78
1940	247	115	86
1941	221	172	166
1942	158	160	133
1943	147	109	106
1944	160	95	63
1945	91	66	32

Table 11. Growth in freshwater.

Smolt Age	Number Examined	Length in inches at end of			Smolt Length in ins.
		1st Year	2nd Year	3rd Year	
1	1	3.6	-	-	6.4
2	74	2.0	4.3	-	4.9
3	1	1.0	3.4	4.7	4.7

Table 12. Mean lengths at the end of the different sea winters.

Age Group (in winters)	Number Examined	Length in inches at end of	
		1st Sea Winter	2nd Sea Winter
1+	45	20.0	-
2	12	18.4	29.7
2+	19	18.6	29.2

Table 13. The annual catches of salmon (and grilse) in the Kerry Blackwater from 1875 to 1945, both years inclusive. (As percentages of the mean annual yield from 1875 to 1945).

Year	1875	1876	1877	1878	1879	1880	1881	1882	1883	1884	1875/84
Catch (%)	128	180	182	88	68	188	147	21	118	95	122
Year	1885	1886	1887	1888	1889	1890	1891	1892	1893	1894	1885/94
Catch (%)	135	170	149	202	177	148	242	134	147	287	157
Year	1895	1896	1897	1898	1899	1900	1901	1902	1903	1904	1895/1904
Catch (%)	176	141	119	114	216	98	90	194	91	25	126
Year	1905	1906	1907	1908	1909	1910	1911	1912	1913	1914	1905/14
Catch (%)	24	38	41	95	158	99	50	37	56	60	66
Year	1915	1916	1917	1918	1919	1920	1921	1922	1923	1924	1915/24
Catch (%)	64	35	88	61	98	30	45	34	75	21	55
Year	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1925/34
Catch (%)	102	74	64	47	8	76	147	92	96	115	69
Year	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944	1935/45
Catch (%)	71	100	43	33	103	212	189	135	126	137	106

1945 - 78%

Calculated Lengths.

The length of each unspawned or " maiden " fish at the end of every year of its life was calculated in the usual way from measurements of the scales, i.e., assuming that the growth of the fish is strictly proportional to the growth of the scale.

River Life. In this section the growth in fresh water will be discussed. Owing to the limited number of observations only the results for the two-year smolt class are significant (see Table 11). The growth rate in the two-year smolt class is similar to that of the same smolt class in the Ballisodare River (see Went, 1941).

Sea Life. The mean lengths at the end of the first and second sea winters have been indicated in Table 12. The grilse appear to be longer on an average than any other age group at the end of the first sea winter. There is slight differentiation in the lengths at the end of the first and second sea winters in the small spring and summer fish, the numbers involved are, however, very small.

Fluctuations in the Yield of this Fishery.

The records of the catches by nets in the Kerry Blackwater are available from the year 1875, and these have been given in Table 13 (as percentages of the average annual catch over the period 1875–1945, both years inclusive). In the first 35 years a draft net and a sweeper net* were used in the fishery, but about 1910 the sweeper net was discontinued owing to the small yields then prevailing. It will be noticed from Fig. 2 that there were considerable fluctuations in the yield. No doubt some of these can be partly attributed to different climatic conditions in the different years. To eliminate the effects of the climatic conditions the 10 years averages since 1875 were calculated, and a smoothed curve showing the results has been added to Fig. 2.

* A form of seine net used with two boats (see " The Irish Pilchard Fishery," Went, 1946.)

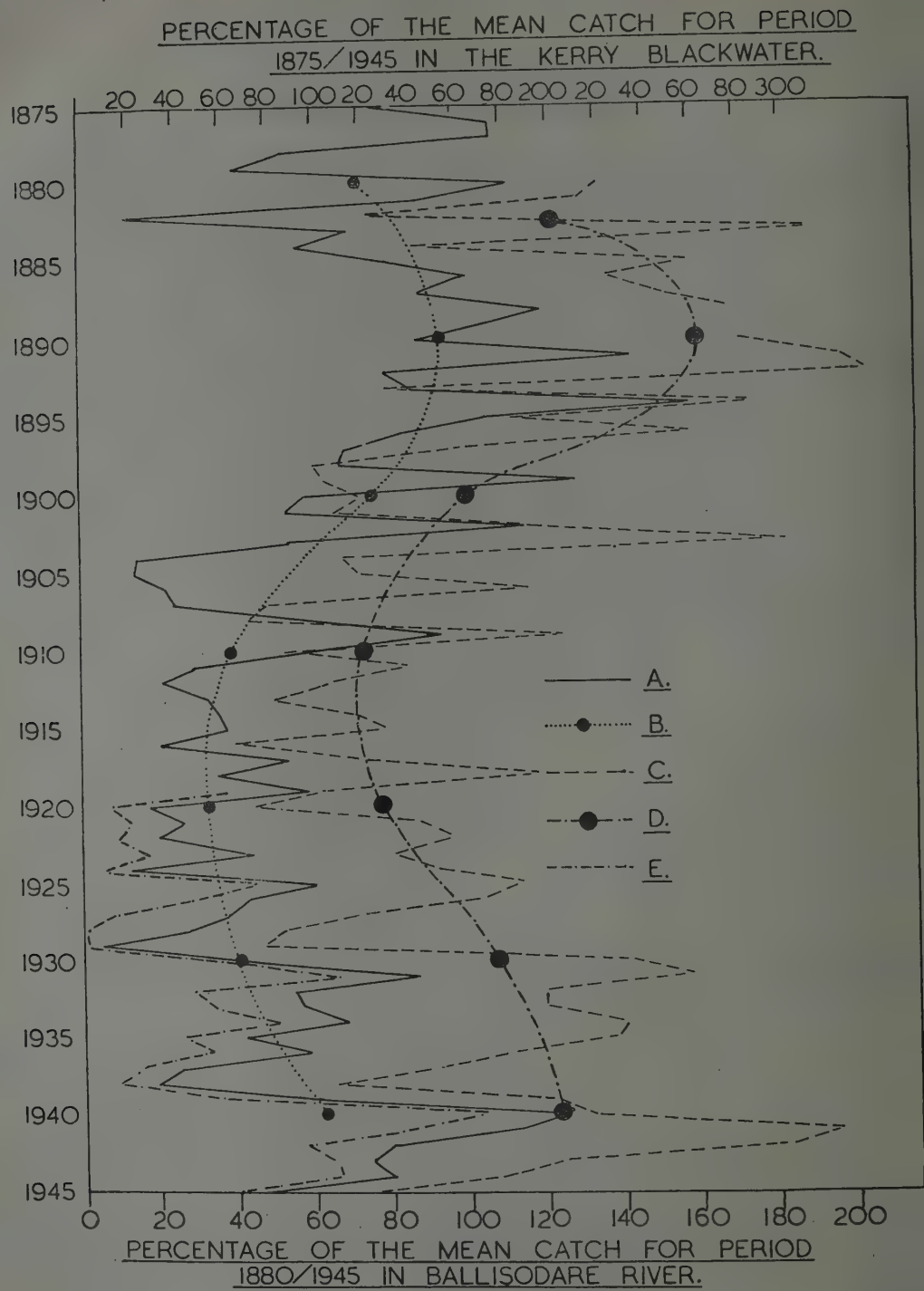

Fig. 2. Fluctuations in the catches in the Kerry Blackwater and Ballisodare River. A = Catches in Kerry Blackwater; B = Smooth curve for Kerry Blackwater based on ten-year averages; C = Catches in Ballisodare River; D = Smooth curve for Ballisodare River based on ten-year averages; E = Catches of grilse in Kerry Blackwater.

This shows that the annual yield increased slightly from 1875/84 to 1885/94 and then decreased until 1915/24, thereafter increasing to date. The latest period, however, has an average yield somewhat less than the 1895/1904, but of course it must be remembered that in the former period a sweeper net had been used. To obtain completely comparable figures an estimate of the yield of the sweeper net would have to be added, in which case the yields in the period 1935/45 would probably exceed those of 1895/1904. There is no reason to believe that there is a permanent decline in the fishery when compared with the early part of the period under review.

From 1920 the actual catches of grilse were recorded and these have been indicated in Fig. 2. It will be seen that the bulk of the fish in the catches were, in fact, grilse.

Records of catch figures in fisheries, such as these, are of great value. It is interesting to compare the present catch figures with those of another river (the Ballisodare River) of the same character as the Kerry Blackwater. In Table 10 the annual figures for both rivers have been indicated as percentages of the mean annual catch from 1924 to 1945. For the sake of comparison some other returns have been added. These are the exports in cwt. from the month of June onwards from Eire since 1924. As mentioned elsewhere (Went, 1938) the exports from June onwards may be regarded as summer fish, and the export returns probably give a reasonably accurate idea of the fluctuations of the quantities of summer fish captured. These export figures are included in *Trade Statistics*, published monthly by the Department of Industry and Commerce, Dublin. Unfortunately we only have the weights (and not numbers), but the export figures for the period may be considered as reasonably comparable. These returns have been plotted in Fig. 3. Generally there is close agreement in the three curves, the most obvious differences being in the export figures for 1926 and the Kerry Blackwater for 1940 and 1944. Whereas the exports and the catches in the Ballisodare River reached a maximum in 1941, this occurred a year earlier in the Kerry Blackwater. It is also noteworthy that in 1927 the catches in the Kerry Blackwater and the Ballisodare Rivers were somewhat below average, whereas in " spring fish " rivers throughout Europe 1927 was a peak year. Grilse (peal) were not particularly plentiful in Ireland in 1927.

Referring again to Fig. 3 it will be seen that the catches in the Kerry Blackwater showed much greater extremes in fluctuations (from 9% in 1929 to 247% in 1940) than were noticed in either the Ballisodare River (41% in 1929 to 172% in 1941) or in the exports (32% in 1945* to 166% in 1941). Why might we ask are there bigger fluctuations in the Kerry Blackwater than in the other two cases ? A complete answer to this question cannot be given but as mentioned earlier about 90% of the fish of any particular year in the Kerry Blackwater have been derived from the brood resulting for a single spawning season. If for any reason the spawning season was bad, a poor yield would probably result after the appropriate interval,

* The proportion of salmon consumed at home was certainly greater in 1945 than in former years so that there is a tendency for the shortage in that year to be over-emphasised

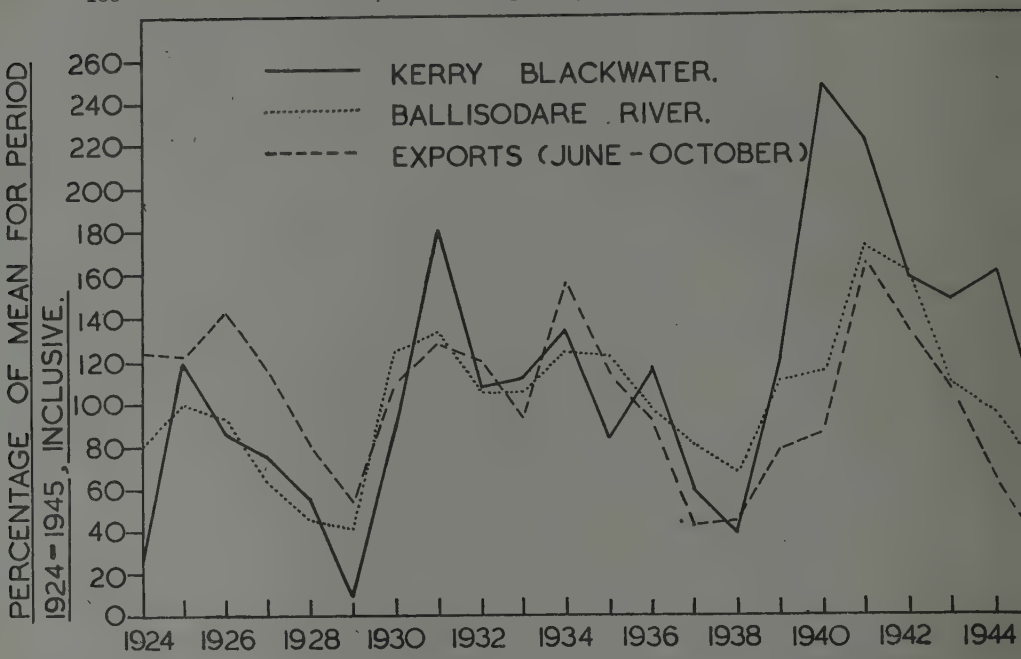

Fig. 3. Fluctuations in the catches in the Kerry Blackwater and Ballisodare River and in the exports of salmon from Eire from June onwards.

and similarly the results of an excellent spawning season would be reflected in the catch of a single year. In the Ballisodare River and in many other fisheries in Ireland there is a tendency for the catch to be spread over two or more brood years (see Went, 1938 to 1946). In other words the " safeguards " of " divided migration and return " are more or less eliminated in a river of the class of the Kerry Blackwater, the " eggs all being in one basket " as it were.

Let us now compare the catches in the Kerry Blackwater with those of the Ballisodare River over a longer period. The appropriate curve for the Ballisodare River has been added to Fig. 2. It will be seen that there is no complete agreement between the curves representing the catches in the Kerry Blackwater and the Ballisodare River over the whole period. If, however, one draws a smooth curve representing the ten-year averages (see Fig. 2) there is a marked similarity between the two sets of observations. In each case a maximum was reached in the period 1885–1894 and a minimum in the period 1905–1925, that for the Ballisodare being somewhat earlier than that for the Kerry Blackwater. From about 1920 onwards there has been a marked increase. It is, therefore, difficult not to accept the conclusion that the catches (and presumably the runs) tend to show some periodicity, and that these fluctuations are independent of artificial alterations produced by man's activities.

The writer wishes to take this opportunity of expressing his thanks to Colonel E. Hood, Dromore Castle, Kenmare, County Kerry, for his kindness in providing the material and data on which this investigation was based.

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No. 21.

EFFECT OF MILD STRAINS OF VIRUS X ON THE YIELD OF UP-TO-DATE POTATO.

By

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Introduction.

Although virus X is the commonest virus attacking potatoes, there has been comparatively little investigation into the effects of this virus on the cropping capacity of the plants. This may be largely due to the fact that many of the most popular commercial varieties, especially in America, are not known in an X-free condition, and therefore the problem has not had a widespread practical significance.

A survey of potato crops in Australia by Bald and Pugsley (2) revealed that the principal commercial varieties grown there were permeated with various strains of virus X. In the course of his investigations, however, Bald (1) discovered a small number of X-free plants of the widely grown Up-to-Date or Factor variety. It then became of interest to determine whether the expected increase in yield of the healthy plants over those which were carriers of X would justify the expenditure necessary to propagate these X-free stocks. The results of a number of experiments extending from 1940 onwards led Bald (3) to the conclusion that the presence of even a masked strain of X causes a significant reduction in yield of tubers, and the policy of multiplying X-free stocks was consequently adopted.

In 1941, Scott (10) stated that the presence of mosaic in Scottish-grown potatoes caused a reduction in yield which varied from 13·3% to 67·3% depending upon the severity of the symptoms; but the diseases studied were not confined to those caused by virus X alone. In 1944, Schultz and Bonde (9) reported that latent mosaic (virus X) reduced the yield of certain American varieties of potato by 9—22%. In the same year, Smith and Markham (11) estimated the comparative yields of healthy and X-infected plants of 9 different varieties of potato at Cambridge, and found a reduction in yield due to the virus of 12%.

In this country, virus-free stocks of such popular varieties as Kerr's Pink, British Queen, Great Scot, Majestic, Arran Banner, Eclipse, etc., have been tested and maintained at the Albert College, Glasnevin, for many years. These nucleus stocks serve as the basis of the foundation seed potato stocks propagated by the Department of Agriculture in accordance with a scheme initiated in 1924. The important variety Up-to-Date was not, however, available in an X-free condition

until recently, when, following the announcement by Bald that X-free stocks existed in Australia, a further search was made in Ireland, and two X-free plants were found in 1943. As the bulk of the Up-to-Date grown in this country is a carrier of X, and is yet on the average one of our best yielding varieties, it was considered of interest to determine to what extent X-free Up-to-Date plants would outyield carrier plants under our conditions. The infection and propagation of the material required two years, so that figures for only one trial are available so far. As these show a somewhat unexpected trend, however, it was decided to furnish a report on the work already carried out.

Experimental Procedure.

In order to obviate the effects of possible agronomic differences between clones, and also with a view to studying the effects of such differences should they exist, it was decided to propagate all the experimental material from single tubers of the two available clones of Up-to-Date. It was also decided, for various reasons, that the infected plants in the trial should be grown from infected tubers rather than inoculated during the trial season, one reason being the difficulty of achieving uniform systemic infection in field inoculated plants. Experience with a severe strain of X has shown that, even when plants are not more than 6 inches above ground at the time of inoculation, individual shoots frequently escape the initial infection, and several weeks may elapse before they contract the disease.

Accordingly, in the spring of 1944 two large X-free tubers were selected, each of which could be cut into 3 sets. The 6 sets were planted in 12 in. pots in an insect-proof glasshouse. One of the plants of each clone was kept as a healthy control, while the remaining two in each case were grafted with scions of Up-to-Date carrying mild strains of virus X. The scions grew vigorously, and the plants were allowed to mature fully before harvesting the tubers. In this way, systemic infection of the tubers was ensured.

Two strains of virus X were employed, both naturally occurring types in Up-to-Date. They will be referred to as strains (*a*) and (*b*), respectively, for the purpose of the present paper. Strain (*a*) may be regarded as a typical mild strain of X. It is carried symptomlessly by Up-to-Date and all other common British varieties, excepting such X-intolerant ones as Epicure and King Edward. In *Datura stramonium* and in tobacco *var.* White Burley it causes a barely discernible light and dark green mottling. The disease was identified as " mottle " in American terminology by Koch and Johnson (8) in 1935. Strain (*b*) is that commonly present in Up-to-Date, and was formerly known as " Up-to-Date Streak " and later as virus B (5). It is carried symptomlessly by Up-to-Date, but when artificially transmitted by grafting it induces top-necrosis in a number of varieties not so affected by typical strains of X. Apart from the latter reaction, however, it behaves as a mild strain of X (6). In those varieties which are tolerant to it it is carried symptomlessly as in Up-to-Date. In *Datura stramonium* and in White Burley tobacco the respective symptoms are a mild mosaic accompanied by slight necrosis and a nebulous ringspot. Koch and Johnson (8) identified the virus content of this Up-to-Date stock as " mottle and ringspot " ; and it is also the opinion of Cockerham (7) that

the material contains a mixture of the top-necrosis strain with a typical mild X strain. For practical purposes, however, the two Up-to-Date sources are carriers of mild strains of X which are distinct from one another although similar in their reactions on Up-to-Date. Both stocks of Up-to-Date have been maintained under glass at Glasnevin for over 20 years as part of the stock laboratory cultures.

In 1945 the produce of the 6 units was grown in a small isolated plot situated amongst beans in a freshly ploughed pasture field. Six tubers of each experimental unit and six of each Up-to-Date source of X were planted in short drills, separated from one another and bounded by drills of X-immune seedling 41956. The drills were manured in the ordinary way with farmyard manure. The plants grew uniformly and were sprayed twice during the season with 2% Burgundy mixture. On July 20th, the plants were tested by inoculation to *Datura stramonium*, and it was found that virus X was present only in those plants which had been grafted with infected scions in the previous year. The tubers were harvested on October 5th, the dead tops having been cut away two weeks previously. Although this plot was intended for purposes of propagation, the yields of tubers obtained from the different units of the two clones are recorded in Table 1, and will be discussed later.

TABLE 1.—YIELDS OF HEALTHY AND X-INFECTED UP-TO-DATE PLANTS, 1945.

		Total yield of 6 plants.	Average yield per plant.	Yield as percentage of healthy.
Clone I	Healthy	24 lb. 6 ozs.	4 lb. 1 oz.	100
	Infected Strain (*a*) ...	24 ,, 8 ,,	4 ,, 1 ,,	100
	Infected Strain (*b*) ...	31 ,, 11 ,,	5 ,, 4 ,,	130
Clone II	Healthy	32 ,, 0 ,,	5 ,, 5 ,,	100
	Infected Strain (*a*) ...	32 ,, 10 ,,	5 ,, 7 ,,	101·9
	Infected Strain (*b*) ...	35 ,, 8 ,,	5 ,, 15 ,,	110·9

YIELD TRIAL 1946.

The majority of tubers obtained from the propagation plot were of ware size and included some very large tubers. The use of whole sets of equal size throughout the trial was impracticable ; cut sets of equal weight were also excluded as it was considered undesirable that any tuber should be cut into more than two portions. The tubers of each healthy clone were therefore graded according to weight and selections made from them in such a way that an equal number of tubers of similar weight was available in the corresponding infected units of the clone. Hence, although the weights of the tuber sets varied in any one lot, the variation was uniform as between healthy and infected lots of the same clone. The weights of the different

grades of set were as follows: Grade A=40—80 grms., Grade B=80—140 grms., Grade C=140—180 grms., and Grade D=180—470 grms. Tubers exceeding 180 grams in weight were cut in two longitudinally, and altogether there were 69 experimental sets of each lot. The numbers of tubers of each grade in the different clones are shown in Table 2.

The experimental plot was situated in a level field which had carried a crop of beans in 1945 and had previously been in grass for 20 years. Each experimental lot was grown in a separate drill, the drills being 30 ins. apart and the plants 18 ins. apart in the drill. The arrangement of the drills is shown below. There were eight experimental drills, including three drills (one healthy and two infected) of each clone, and a drill each of the Up-to-Date sources of the X strains (*a*) and (*b*). To obviate border effects three extra plants were grown at the ends of the drills, and these were neglected at digging time. In addition, a drill of healthy Majestic plants separated the healthy and the infected lots of each clone, while the plot was bordered on either side by two more drills of healthy plants, making in all 17 drills of 75 plants each. The remainder of the field was sown with a mixture of oats and legumes for ensilage.

ARRANGEMENT OF DRILLS IN FIELD PLOT, 1946.

1. Up-to-Date. Healthy.
2. Epicure. Healthy.
3. Majestic. Healthy.
4.* Up-to-Date. Healthy. Clone I.
5.* Up-to-Date. Healthy. Clone II.
6. Majestic. Healthy.
7.* Up-to-Date infected Strain (*a*). Clone I.
8.* Up-to-Date infected Strain (*a*). Clone II.
9. Majestic. Healthy.
10.* Up-to-Date infected Strain (*b*). Clone I.
11.* Up-to-Date infected Strain (*b*). Clone II.
12. Majestic. Healthy.
13.* Up-to-Date. Source of Strain (*a*).
14.* Up-to-Date. Source of Strain (*b*).
15 Majestic. Healthy.
16. Epicure. Healthy.
17. Up-to-Date. Healthy.

* Experimental drill.

The drills were manured with farmyard manure and the usual artificials and the sets planted on April 11th. On May 12th when most of the plants were above ground, a sharp frost occurred which caused scorching of the foliage in scattered plants throughout the plot. No plant was seriously injured, however, and following rain in the latter part of May the plants grew extremely vigorously. There had been no "misses," and there was a complete absence of root troubles such as

Blackleg (*Bacillus phytophthorus*). No difference whatever was apparent between the healthy and infected plants, and by the middle of June the uniformly healthy and vigorous appearance of all the experimental plants was remarkable. About the end of June, however, when the plants were in full flower, a conspicuous yellowish hue developed in the tops of 3 adjacent plants in Drill 11 (Clone II infected X strain (*b*)), and shortly afterwards the same chlorotic effect appeared in contiguous plants in the same drill. In these the yellowing appeared first in one or two shoots and then spread gradually through the plant, eight plants altogether showing definite chlorosis. Owing to the manner of its appearance and the fact that it was strictly confined to one spot, the effect was at first thought to be due to some unknown soil factor operating in this particular part of Drill 11. There was no trace of rolling in the lower leaves at first, but slight rolling did occur eventually, and in the meantime grafts of scions from the affected plants to healthy President potatoes demonstrated conclusively that the condition was primary leaf roll. A close watch was kept on the remaining drills, but no further leaf roll could be detected during the season, nor was there any difference in appearance between the healthy and X-infected plants generally.

On July 2nd, the plot was sprayed with 2% Burgundy mixture. At this period growth was luxuriant, but from July onwards the weather became abnormally wet with very little sunshine, and the plants were buffeted by wind and rain, especially by a severe rainstorm which occurred on August 12th. The unfavourable effect of such conditions on aphids probably explains why the leaf roll failed to spread from the initial point of infection. Blight (*Phytophthora infestans*) had not yet appeared at the time of the second spraying on July 29th, but began to develop towards the end of August, and became widespread during September. The application of a third spray in August was impossible owing to the tangled state and brittle nature of the stalks. Early in October the plants were completely dead, and harvesting took place on October 25th. The tubers were taken indoors and brushed by hand to remove loosely adhering soil before being weighed. The weights of ware, seed, and chats, in each grade were taken, as well as the total yield of tubers in each grade. Notwithstanding the severity of Blight attack on the foliage the number of tubers showing blight lesions was negligible. This was probably due to the fact that the onset of the disease was late and its progress rapid.

During the latter half of July the absence of virus X in plants of Drills 4 and 5 was confirmed by inoculation to *Datura stramonium*. The plants were tested in groups of five, a single leaf being taken from each plant. It had previously been ascertained that inoculum prepared by grinding up as many as nine healthy leaves with one infected one could be relied upon to produce symptoms of X in *Datura*. In addition, several scions were taken at random from the same drills, and these failed to produce symptoms when grafted on healthy Epicure potato in the glasshouse.

TABLE 2

COMPARATIVE YIELDS OF HEALTHY AND X-INFECTED UP-TO-DATE POTATO PLANTS 1946.

	Grade of set	No. of plants	Ware lbs.	Ware oz.	Seed lbs.	Seed oz.	Chats lbs.	Chats oz.	Total yield lbs.	Total yield oz.	Av. Yield per plant lbs.	Av. Yield per plant oz.	Yield as percentage of healthy
CLONE I.													
Healthy	A	12	29	6	9	3	1	3	39	12	3	5	
	B	17	45	8	13	2	2	9	61	3	3	9	
	C	14	39	12	9	0	2	11	51	7	3	11	
	D	26	55	14	21	4	4	0	81	2	3	1	
Totals		69	170	8	52	9	10	7	233	8	3	6	100
Infected Strain (*a*)	A	12	30	15	5	9	0	4	36	12	3	1	
	B	17	35	8	14	2	4	0	53	10	3	2	
	C	14	35	8	12	6	2	15	50	13	3	10	
	D	26	59	0	21	12	5	8	86	4	3	5	
Totals		69	160	15	53	13	12	11	227	7	3	4	97
Infected Strain (*b*)	A	12	35	5	4	4	0	7	40	0	3	5	
	B	17	39	8	16	4	9	2	64	14	3	13	
	C	14	32	9	16	12	7	2	56	7	4	¼	
	D	26	80	10	18	0	4	10	103	4	3	15	
Totals		69	188	0	55	4	21	5	264	9	3	13	113
CLONE II.													
Healthy	B	11	32	0	7	7	2	1	41	8	3	12	
	C	4	10	4	4	10	1	8	16	6	4	1½	
	D	54	153	10	27	10	12	7	193	11	3	9	
Totals		69	195	14	39	11	16	0	251	9	3	10	100
Infected Strain (*a*)	B	11	22	10	5	8	1	6	29	8	2	11	
	C	4	11	0	3	14	1	0	15	14	3	15½	
	D	54	176	15	32	0	8	3	217	2	4	0	
Totals		69	210	9	41	6	10	9	262	8	3	13	104
Infected Strain (*b*)	B	11	45	12	2	12	1	9	50	1	4	9	
	C	4	9	0	5	2	1	7	15	9	3	14	
	D	54	100	10	33	2	16	0	149	12	2	10	
Totals		69	155	6	41	0	19	0	215	6	3	2	86
UP-TO-DATE SOURCES OF X STRAINS (a) AND (b).													
Strain (*a*)	A	12	26	14	5	10	0	15	33	7	2	12	
	B	17	34	9	18	8	5	13	58	14	3	7	
	C	14	29	5	16	2	4	14	50	5	3	9	
	D	26	68	15	21	3	8	14	99	0	3	13	
Totals		69	159	11	61	7	20	8	241	10	3	8	103
Strain (*b*)	A	12	28	4	5	9	1	13	35	10	2	15	
	B	17	37	0	16	0	7	2	60	2	3	8	
	C	14	25	8	16	0	7	6	48	14	3	8	
	D	26	73	0	25	12	10	12	109	8	4	3	
Totals		69	163	12	63	5	27	1	254	2	3	10	108·8

DISCUSSION OF RESULTS.

The total yields of tubers and the yields from the different grades of set are shown in Table 2. The amounts of ware, seed, and chats are shown in the same table. Taking Clone I it will be seen that the average yield per healthy plant was 3 lb. 6 oz. (equivalent to 17½ tons per statute acre); that strain (*a*) infected plants yielded 3% less than the healthy, while strain (*b*) infected plants out-yielded the healthy by 13%. The Up-to-Date stocks which were the sources of the infecting strains, and of which the sets were graded to correspond with those of Clone I, outyielded the healthy plants of Clone I by almost 9% in the case of strain (*a*) and by 3% in the case of strain (*b*) stock.

In the case of Clone II, the average yield per healthy plant was 3 lb. 10 oz. (18½ tons per acre); strain (*a*) infected plants outyielded the healthy by 4%, while strain (*b*) infected plants produced 14% less than the healthy. It will be noted, however, that it was in the latter group that the primary leaf roll appeared, and examination of Table 2 shows that the reduced yield occurred amongst the plants of Grade D in which group the leaf roll was found. Actually, for ease in handling, the tubers of this grade had been dug and weighed in two sections, and this narrowed down the low yielding section to the last 27 plants of the drill which included those infected with leaf roll. Furthermore, the drop in yield in this section occurred exclusively in the ware size tubers, the weights of seed size tubers and chats from these 27 plants being greater than that of either healthy or strain (*a*) infected plants of the same clone. It seems evident, therefore, that the primary leaf roll effected a pronounced reduction in yield, and that there is no justification on the basis of these figures for assuming that any significant reduction in yield was caused by the (*b*) strain of virus X. The only other case of reduced yield, that of 3% in the (*a*) infected plants of Clone I, is counterbalanced by an increase of the same order in the corresponding plants of Clone II. Assuming that leaf roll was mainly responsible for the drop in yield in the strain (*b*) infected plants of Clone II, the general inference to be drawn from the results is that no significant reduction in yield is caused by the mild strains of X employed, but that there may even be an increase in yield due to the infection under certain conditions.

It is obvious, however, that yield trials of this type must be carried out over a number of seasons in order to compute the effects of varying weather conditions. In this particular experiment what promised to be a magnificent crop was marred by the abnormal rainfall; the average weight of tubers per plant was 3 lb. 8 oz., whereas the appearance of the crop in mid-summer justified an expectation of at least 5 lb. per plant, given normal weather conditions throughout the season. Furthermore, although the killing of maincrop plants by Blight in September or early October is a usual occurrence in this climate, in a season of average rainfall senescence would be well advanced at this period, and the effect of the disease on yield comparatively slight. In 1946, however, the continuous wet weather in August retarded senescence, so that the death of the plants in September due to Blight attack was definitely premature. It might reasonably be suggested that if the plants had matured normally the comparative yields of healthy and infected ones would have been different. In this connection, however, the yields obtained from the 1945

propagation plot (Table 1) are of interest. The sets used in this plot were the selected produce of pot plants and were all uncut and approximately 80—100 grms. in weight. Throughout the season, the plants presented an appearance of uniform vigour and health, and owing to dry weather conditions in late summer Blight attack was comparatively mild. The average yield per plant was 5 lb., which is equivalent to almost 26 tons per statute acre. It will be seen that the strain (*a*) infected plants of each clone gave practically the same yield as the corresponding healthy plants, while the strain (*b*) infected plants outyielded the healthy, in one case by the substantial margin of 30%. Owing to the small numbers of plants involved it cannot be claimed that these figures are truly representative; but at least they suggest that in a season of average rainfall in this country the yielding capacity of Up-to-Date is not adversely affected by the presence of mild strains of X.

Whether or not the results of future experiments in different weather conditions continue to show the same trend, the fact emerges that plants infected with mild strains of X may sometimes outyield healthy plants of the same clone. So far, no confirmation of this tendency is to be found in the results of other investigators; but comparatively few trials have been carried out and, apart from differences in the strains of X employed, growth conditions vary at the different centres where such trials have been made. Scott's (10) experiment, although performed under conditions which probably approximated closely to those at Glasnevin, is not comparable with the present one, for he was concerned with the effect on cropping capacity of mosaic diseases in general, irrespective of the underlying viruses; his "negligible mottle" might have been due either to virus A or virus X, and his control plants, according to Smith and Markham (11), were probably carriers of latent X. The writers' experiment would be more or less equivalent to that of Smith and Markham (11), who also estimated the effect on yield of a mild strain of X, were it not for the fact that Smith and Markham inoculated their experimental plants in the field, whereas at Glasnevin the diseased plants were grown from infected sets. Experience here with a severe strain of X has shown that symptoms are invariably more severe following initial infection with the virus than at any subsequent stage of the host plant's growth; this effect is also apparent, although less obvious, in the case of milder strains of X. As it is possible, therefore, that yields would be affected differently according to the time of infection of the plants, the experiments at Glasnevin and Cambridge are not strictly comparable.

Schultz and Bonde (9) found consistent reductions in yield due to virus X infection in American varieties of potato. The disease tested was "common latent mosaic," which probably corresponds to some extent with the (*b*) strain of X used in the present work; but it is doubtful whether in general the virus strains underlying this disease are as mild as those used here. In the case of commercial Green Mountain, of which no healthy stock is available, Schultz and Bonde refer specifically to a weak strain of X which they tested against "common latent mosaic" in the same variety. The weak strain outyielded the other by 9%, which was similar to the difference in yield of healthy and common latent mosaic-infected Green Mountain Seedling. From this result one might infer that the weak strain probably had no significant effect on the yield of commercial Green Mountain.

Bald (3) demonstrated conclusively that under Australian conditions infection with different mixtures of X strains depresses the yields of Up-to-Date and other varieties of potato to an extent commensurate with the severity of the strains involved. He also observed that different clones of X-free Up-to-Date differed significantly in yielding capacity. On comparing the yields of X-free and X-infected Up-to-Date (4) he found in two experiments a reduction in yield due to the infection, although in only one case was the difference significant. In one small experiment, Bald (3) worked specifically with a very mild strain of X in a variety believed to be Great Scot, and found that the infected plants yielded 10% less than the healthy. Unfortunately growth conditions in this experiment were very unfavourable owing to excessive dryness, with the result that yields of both healthy and infected plants were exceedingly small.

While the results of other investigators demonstrate clearly that various strains of X reduce the cropping capacity of potatoes to a degree proportionate to the severity of the strain involved, the evidence relating specifically to the effects of mild strains of X is meagre. The logical assumption is, however, that such strains also depress yields, if only to a slight extent; the finding of an increase in yield due to infection is, therefore, difficult to explain. There is some evidence, however, that infection with virus X hastens maturity (3), (10), which presumably implies an earlier initiation of tuber formation; and Bald's (4) experiments show that the falling off in yield of infected plants is due to a reduction in the rate of tuberation in the final stages of growth. If it were a fact that infection with a mild strain of X induced earlier tuber formation it is conceivable that, in a climate in which crops are killed more or less prematurely by Blight or frost, such an effect might more than offset a slight reduction in the rate of tuberation in the senescent stage; thus, the yields of infected plants might be equal to, or greater than, those of healthy plants. It does not follow that a simliar compensation would occur in the case of stronger strains of X, as the effect on time of tuber initiation might not be related to severity of strain in the same way as is the effect on rate of tuber formation.

The restricted incidence of leaf roll in the yield trial at Glasnevin serves to illustrate the serious effect on yield of the primary phase of this disease. It is clear that complete freedom from leaf roll must be aimed at in testing the comparative yields of healthy and X-infected plants, and herein lies one of the difficulties of conducting such trials on a large scale. Constant supervision is necessary, and the more extensive the plot the more danger there is that primary leaf roll may pass undetected, with a consequent unsuspected interference with the validity of the results.

SUMMARY.

A field trial was conducted to determine the effect of two different mild strains of virus X on the cropping capacity of Up-to-Date potato. Both strains were naturally occurring ones which are carried symptomlessly in Up-to-Date. Two clones of Up-to-Date were tested, from single tubers of which all the experimental plants were derived.

Weather conditions favoured luxuriant growth of the experimental plants during the first half of the season, but abnormal rain and lack of sunshine retarded senescence, and the plants were killed prematurely by Blight (*Phytophthora infestans*).

The average yield of tubers per healthy plant was 3 lb. 8 oz., which is equivalent to 18 tons per statute acre. Strain (*a*) infected plants of Clone I yielded 3% less than the healthy, but those of Clone II outyielded the healthy by 4%. Strain (*b*) infected plants of Clone I outyielded the healthy by 13%, but those of Clone II yielded 14% less than the healthy. This reduction, however, was obviously due to an outbreak in mid-season of primary leaf roll, which was restricted to a number of adjoining plants in one particular drill. Neglecting the latter figure, the results in general indicated that no significant reduction in yield was caused by the latent strains of X employed, the tendency being rather towards an increase in yield due to the infection. The yields from a small propagation plot of the same Up-to-Date stocks in the previous season showed a similar trend.

The results are discussed and compared with those of other investigators.

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No. 22.

STUDIES ON UREIDES. PART 3.

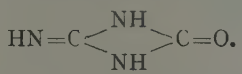
(a) Constitution of Hallwachs' Acid.
(b) A New Copolymer of Cyanamide and Cyanic Acid.

By

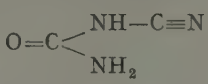
A. E. A. WERNER.

[Read March 25. Published separately July 9th, 1947).

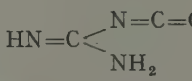
By the hydrolysis of dicyandiamide in dilute barium hydroxide solution Hallwachs (1) obtained in small yield a compound to which he gave the name amidodicyanic acid, and for which he proposed the cyclic structure



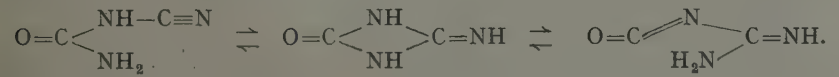
He also synthesised the potassium salt of the same substance in good yield directly from cyanamide and potassium cyanate. Baumann (2) showed that the compound could be hydrolysed on heating with dilute acids to give biuret ; later Wunderlich (3) confirmed this observation and on the strength of it proposed the structural formula.



This so-called cyanurea structure has in the course of time gained general acceptance. Recently, however, Blair and Smith (4) offered for consideration a new formula, namely guanyl isocyanate,



They were led to propose this formula in order to account for their observation that guanidine and urea are produced along with biuret during acid hydrolysis. They maintained that the cyanurea formula could not account for the formation of either urea or guanidine, and suggested that the chemistry of Hallwachs' acid was best explained by the assumption of tautomerism between a four-membered ring and two different chain structures as indicated below :—



The new formula proposed by Blair and Smith (*loc. cit.*) lays itself open to the serious criticism that a compound possessing such a structure would not be expected to show acidic properties, but should instead show basic properties, since it contains a free guanidino group. Furthermore, since urea was only detected qualitatively, and guanidine could only be isolated in a very small yield, these substances must be regarded as by-products of the main hydrolysis, and therefore their formation hardly warrants the acceptance of a new formula. It is therefore proposed to retain the cyanurea formula for Hallwachs' acid, and to present experimental evidence in support of a mechanism of the hydrolysis which will account for the production of urea and guanidine as by-products of the main reaction.

The necessary clue leading to the elucidation of the mechanism of hydrolysis, which provides a reasonable explanation of the formation of urea and guanidine was the discovery that cyanamide could be detected during the *initial* stages of the hydrolysis. It is suggested that the primary reaction in the hydrolysis is the dissociation of the cyanurea molecule into cyanamide and cyanic acid, (1) thus :—

$$O{=}C\begin{<}{NH{-}C{\equiv}N \atop NH_2} \longrightarrow H_2N{-}C{\equiv}N + HN{=}C{=}O.$$

The cyanamide undergoes hydration to urea, which combines with cyanic acid to produce biuret. The yield of biuret is, however, well below the theoretical because much of the cyanic acid undergoes hydrolysis forming ammonium salts. Guanidine can be formed as the result of the union of some cyanamide with the ammonium salts, thus,

$$H_2N{-}C{\equiv}N + NH_4X \longrightarrow [C(NH_2)_3]^+ + X^-$$

in accordance with the method for the preparation of guanidine salts described by Werner (E. A.) and Bell (5). This theory of the mechanism is in agreement with the fact that the hydrolysis of Hallwachs' acid in dilute acid solution is a slow process ; the initial dissociation is the rate-determining reaction, and direct addition of the elements of water to the —CN group does not occur. However biuret can be produced in good yield by the direct hydration of cyanurea by dissolving it in the cold in concentrated sulphuric acid, allowing to stand at room temperature, and then pouring into ice-cold water. (It is also shown that the same technique can be used to bring about the direct hydration of dicyandiamide to guanylurea [dicyandiamidine]). This direct hydration to give biuret affords further evidence in support of the cyanurea structure.

The theory outlined above was confirmed by an investigation of the action of nitrous acid on Hallwachs' acid. Cyanamide was detected qualitatively in the initial stages of the reaction, and the residual solution was found to contain ammonia. A quantitative determination of the ratio of the volumes of carbon dioxide and nitrogen evolved under different experimental conditions was found to be in agreement with the following theory of the course of the reaction :—

$$\text{Phase I. } O{=}C\begin{<}{NH{-}C{\equiv}N \atop NH_2} + HNO_2 \longrightarrow N_2{+}CO_2{+}H_2O{+}H_2N{-}C{\equiv}N$$

[1] Although Blair and Smith (*loc. cit.*) detected the formation of cyanic acid by its pungent odour, they failed to detect any cyanamide.

(a) $H_2N-C\equiv N + HNO_2 \longrightarrow N_2 + H_2O + HN=C=O$

Phase II. (b) $HN=C=O + H_2O + HX \longrightarrow NH_4X + CO_2$

(c) $HN=C=O + HNO_2 \longrightarrow N_2 + CO_2 + H_2O$

If the concentration of free mineral acid is high, reaction (b) will be favoured; whereas if the concentration of mineral acid is low and that of nitrous acid moderately high, reaction (c) will be favoured. Hence it follows that under experimental conditions so chosen that the concentration of mineral acid is high the overall reaction may be represented by the following equation :—

$$O=C\begin{<}{NH-C\equiv N}{NH_2} + 2HNO_2 + HX \longrightarrow 2N_2 + 2CO_2 + NH_4X + H_2O$$

so that the volumes of carbon dioxide and nitrogen will be equal. On the other hand in the presence of an excess of nitrous acid an additional source of nitrogen is introduced so that the ratio of the volume of nitrogen to that of carbon dioxide will approach the theoretical ratio of 1.5 required by the following equation :—

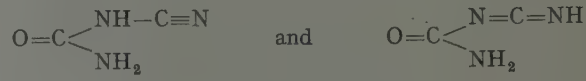
$$O=C\begin{<}{NH-C\equiv N}{NH_2} + 3HNO_2 \longrightarrow 3N_2 + 2CO_2 + 3H_2O.$$

The above considerations are borne out by the experimental results collected in Table 1, particularly the fact that in the presence of acetic acid and excess nitrous acid the ratio is very nearly equal to the theoretical required. On the other hand when hydrochloric acid is used to generate the nitrous acid, reaction (b) is never completely suppressed, and intermediate values for the ratio are obtained.

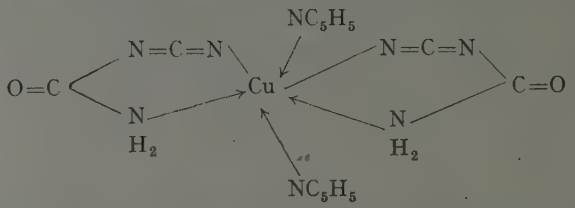
TABLE 1. THE ACTION OF NITROUS ACID ON CYANUREA.

Cyanurea millimols	Sodium Nitrite millimols	Acid added	Volume of Nitrogen c.c.	Volume of Carbon Dioxide c.c.	Ratio N_2 / / CO_2
1	2	2 c.c. NHCl	17.0	13.3	1.28
1	2	3 c.c. NHCl	29.9	21.4	1.12
1	2	1 c.c. 30% HCl	26.8	26.0	1.03
1	3	1 c.c. 30% HAc	13.8	9.4	1.47
1	4	1 c.c. 30% HAc	16.5	11.2	1.48
1	1	3 c.c. NHCl	10.7	10.95	0.99

A further point worthy of mention in connection with the structure of cyanurea is the fact that the phenomenon of tautomerism must play an important part in stabilising the molecule. Neglecting tautomerism in the acid amide part of the molecule there are still two possible tautomeric structures, namely,

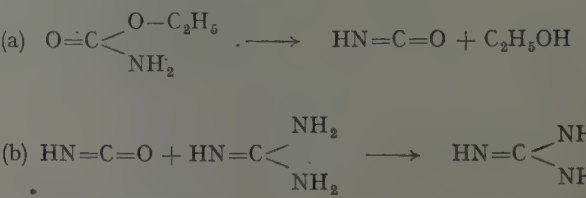


The imino tautomer is most probably the form from which the covalent heavy metal salts are derived, and this idea receives additional support from the preparation of a new deep blue copper pyridine salt corresponding to the formula, $(C_2H_2N_3O)_2Cu.2C_5H_5N$, and having the probable chelate structure shown below :—



The second part of the present communication is concerned with an interesting substance which is isomeric with Hallwachs' acid, but yet possesses entirely different chemical and physical properties. It seems probable that this substance was originally obtained by Wunderlich (*loc. cit.*) as the result of the action of heat on guanolin (carbethoxyguanidine), and later by Soll and Stutzer (6), who make a passing reference to the formation during the thermal decomposition of guanylurea of a white insoluble material, the analysis of which approximated to that required for $C_2H_3N_3O$. However neither the chemical nor physical properties of this substance are described in either of the above mentioned papers, Wunderlich (*loc. cit.*) merely stating that it is entirely different from the isomeric compound obtained by Hallwachs (*loc. cit.*).

It is now shown that when guanylurea hydrochloride is heated to 175°C. it decomposes completely in twenty minutes giving ammonium chloride and this new substance in 90% yield together with a small amount of ammelide. The same substance is also obtained by the action of heat on an equimolecular mixture of guanidine carbonate and urethane. This latter reaction was originally described by Bamberger (7) as a method for the preparation of guanylurea, which was supposed to be formed as the result of the following sequence of reactions :—



In a repetition of Bamberger's work attempts to isolate any guanylurea *via* its characteristic red copper salt were unsuccessful this is, however, not altogether

surprising, since Werner (E. A.) (8) has shown that urethane only dissociates to a very small extent even at its boiling point (187°C.). Therefore the formation of guanylurea according to the above series of reactions must be regarded as extremely unlikely. As shown in the experimental part the reaction between urethane and guanidine carbonate leads instead to the intermediate formation of guanolin :—

$$O{=}C\begin{<}{O{-}C_2H_5 \atop NH_2} + HN{=}C\begin{<}{NH_2 \atop NH_2} \longrightarrow NH_3 + HN{=}C\begin{<}{NH{-}CO{-}O{-}C_2H_5 \atop NH_2}$$

Guanolin can be isolated from the reaction mixture if the temperature does not rise above 110°C., but at the temperature of 150°C. used by Bamberger (*loc. cit.*) the guanolin decomposes as rapidly as it is formed with the evolution of ethyl alcohol vapour, and the new compound is formed. This reaction mechanism receives further support from the observation that the ammonia evolution occurs at a lower temperature (70° C.) than the evolution of ethyl alcohol vapour, which only starts at 120°C., i.e. above the decomposition point of guanolin.

Attention was also directed to the chemical reaction resulting from the action of heat on an equimolecular mixture of urea and guanidine carbonate. This reaction was first investigated by Smolka and Friedreich (9), who claimed that it led to the formation of diguanylbiuret (diiminotetruret) of the formula, $H_2N{-}C(NH){-}NH{-}CO{-}NH{-}CO{-}NH{-}C(NH)NH_2$. There are however two cogent reasons for doubting the accuracy of the claim put forward by these workers. Firstly the properties ascribed by Smolka and Friedreich (*loc. cit.*) to the supposed diguanylbiuret are exactly those possessed by the new compound (*vide infra*), and secondly convincing evidence has been recently presented by Werner and Gray (10) to show that the existence of the compound tetruret itself must be regarded as extremely doubtful. In point of fact it is now shown that when equimolecular amounts of urea and guanidine carbonate are heated to about 130°C. the new compound is obtained in almost quantitative yield.

Since the properties of this new substance have not been previously described, certain of its more important features are detailed below in order to provide evidence in support of a suggested structure for the substance :—

(a) The compound does not show any true melting point ; on heating to about 450°C. decomposition takes place with the evolution of ammonia and cyanic acid vapour, which form a sublimate of ammonium cyanate in a cooled receiver, some melamine is deposited on the walls of the test-tube and a golden yellow residue of melon remains. The formation of these decomposition products may be explained on the assumption that the compound breaks up initially into cyanamide and cyanic acid. The cyanamide polymerises to the trimeric melamine, which at the higher temperature loses ammonia to form melam, which in turn is finally converted into the stable melon.

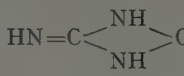
(b) The compound is insoluble in water and the usual organic solvents, but dissolves to a small extent in formamide on warming.

(c) The compound shows amphoteric properties, dissolving in acids to give salts of the general formula $C_2H_3N_3O.HX$, and in alkalies to give salts of the general formula $M.C_2H_2H_3O$, which are decomposed to the parent substance by carbon

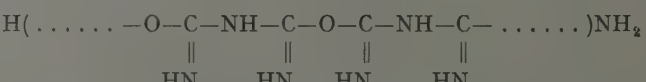
dioxide. It does *not* dissolve in concentrated ammonium hydroxide. A silver salt was also prepared and found on analysis to have the empirical formula $AgC_2H_2N_3O$.

(d) The compound is chemically rather inert; it resists the oxidative action of alkaline hypobromite, and its resistance to hydrolysis is exemplified by the fact that its solution in N potassium hydroxide can be refluxed for ten hours without undergoing appreciable decomposition.

The above chemical and physical properties are definitely not in agreement with the idea that this new compound possesses the cyclic structure

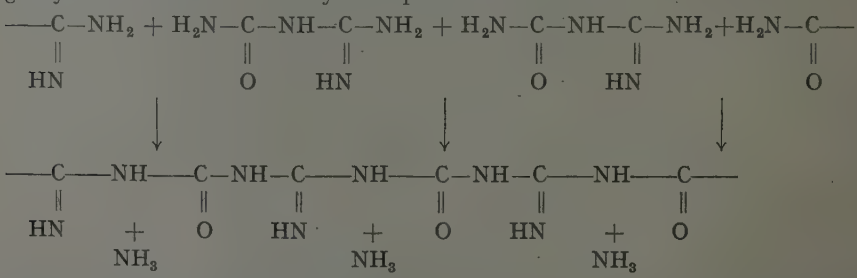


which was proposed by Wunderlich (*loc. cit.*). They suggest rather that the compound has a high molecular weight, and, in accordance with the theoretical considerations established by Carothers (11) which indicate the improbability of the formation in bifunctional condensation reactions of rings containing more than eight atoms, it seems that an open chain structure is the most likely one. Since the compound contains cyanic acid and cyanamide in equimolecular proportions it is suggested that it is best represented as a macromolecular *linear copolymer* of cyanic acid and cyanamide, namely :—



The exact nature of the terminal groups is unknown, but, bearing in mind the experimental conditions under which the copolymer is produced, it is probable that the addition of a molecule of ammonia occurs, giving an —OH group at one and an $—NH_2$ group at the other end of the chain, as indicated in the above formula. A similar open chain structure has also been advanced for cyamelide, the low temperature polymer of cyanic acid. (*Vide* Sidgwick's Organic Chemistry of Nitrogen, 2nd edition, p. 323.).

The actual formation of the copolymer takes place as the result of a polycondensation involving the *intermolecular* elimination of ammonia between the guanido group of one molecule and the carbamino group of a second molecule of guanylurea. The reaction may be represented as follows :—



The alternative formation of the copolymer from guanolin may be similarly represented as a polycondensation reaction involving the intermolecular elimination of ethyl alcohol between the guanido group of one molecule and the carbethoxy

group of a second molecule of guanolin. It is of incidental interest to contrast these reactions with the thermal decompositions of the urea analogues, ethyl allophanate and biuret. The former decomposes on heating above its melting point (190°C.) forming cyanic acid, which undergoes polymerisation to the cyclic cyanuric acid; while Werner (E. A.) (12) has shown that biuret decomposes in a complex manner leading to the formation of cyanuric acid and ammelide, which also has the stable 1, 3, 5,-triazine ring structure. This same ring system is also present in melamine, the trimeric polymer of cyanamide, and in ammeline, which may be regarded as a condensation product of cyanic acid and cyanamide in the ratio of 1 : 2. It is thus clear that the new copolymer described in the present communication is of particular interest, because it represents a unique example of a linear condensation product of cyanamide and cyanic acid. Owing to the insolubility of the substance in appropriate solvents it is unfortunately impossible to determine the number of repeating units in the chain, but its physical character would indicate that the number of such units is quite large, as is known to be the case with the polyoxymethylenes, in which Staudinger and his associates (13) have shown that the chain contains from forty to one hundred units.

EXPERIMENTAL.

Hydrolysis of Cyanurea. A solution of cyanurea (4.25 g.) in *N*/2 sulphuric acid (100 c.c.) was heated slowly on a water-bath; as the temperature rose test portions of the solution were withdrawn and examined for the presence of cyanamide. At 70°C. the presence of cyanamide was detected by the characteristic pale yellow precipitate of silver cyanamide insoluble in ammonium hydroxide solution. The solution was refluxed at 80°C. for 90 minutes, during which the characteristic odour of cyanic acid was noticeable. The solution was allowed to cool and was titrated with *N* sodium hydroxide. Volume required was 30 c.c. Hence the amount of ammonia produced as a result of the hydrolysis of cyanic acid is equivalent to 40 c.c. of *N*/2 sodium hydroxide corresponding to 40% of the theoretical.

The above experiment was repeated, and the resulting solution was rendered alkaline by the addition of a small volume of concentrated sodium hydroxide solution, and aerated until all the ammonia had been expelled. The solution was then concentrated to a small bulk under reduced pressure. The crystalline material which separated was filtered and recrystallised from ethyl alcohol. M.P. 188°C. not depressed by mixing with an authentic specimen of biuret. Weight=1.05 g. equivalent to 20% of the theoretical. Guanidine was found to be present in the filtrate in small amount, being identified by means of its picrate. M.P. 310°C.

Action of Nitrous Acid on Cyanurea. All experiments were carried out in a Lunge nitrometer filled with mercury, and the following technique was employed. One millimolecular proportion (0.085 g.) of cyanurea and the requisite quantity of recrystallised sodium nitrite dissolved in distilled water (2 c.c.) were introduced into the nitrometer. The nitrometer cup was rinsed out with distilled water (1 c.c.), the required amount of acid was introduced into the nitrometer, and the total volume of the solution was adjusted to a volume of 6 c.c. by adding distilled water if required. Except in those experiments in which acetic acid was used the evolution

of gas was fairly brisk. The experiment was allowed to continue for 18 hours. The total volume of gas in the nitrometer was noted, and the gas was analysed for (i) carbon dioxide by noting the contraction in volume resulting upon the addition of concentrated solution of sodium hydroxide, and (ii) nitric oxide by noting the contraction in volume after the addition of a strong solution of potassium permanganate. The residual gas in the nitrometer was assumed to be nitrogen. All gas volumes were reduced to N.T.P., and a suitable allowance was made for the volume of carbon dioxide which remains dissolved in the aqueous solution.

Preparation of a Copper Pyridine salt from Cyanurea. To an aqueous solution of the potassium salt (1.14 g.) were added pyridine (3 c.c.) and a 5% solution of cupric sulphate (25 c.c.). On standing for a few hours deep blue acicular crystals gradually separated out of the solution. The crystals were dried in a desiccator over sulphuric acid. On ignition 0.1228 g. gave 0.0248 g. CuO, equivalent to Cu=16.10 per cent. $(C_2H_2N_3O)_2Cu.2C_5H_5N$ requires Cu=16.19 per cent.

Direct Hydrolysis of Cyanurea and Dicyandiamide. (i). To concentrated sulphuric acid (20 c.c.) cooled to −10°C. was added in small portions cyanurea (5 g.), the rate of addition being such that the temperature did not rise above 0°C. The cyanurea dissolved without effervescence giving a clear solution. A test portion of the solution was found to give the biuret reaction when poured into water and tested in the usual manner. The main solution was allowed to stand at room temperature for one hour, and was then poured with vigorous stirring on to crushed ice (ca.100 c.c.). The resulting solution was treated with solid barium carbonate until neutral, the barium sulphate was removed, and the filtrate was evaporated to a small bulk under reduced pressure. The crystalline material which separated was filtered off and recrystallised from ethyl alcohol. Weight=4.5 g. corresponding to 75 per cent. of the theoretical. M.P. 190°C. not depressed by admixture with an authentic specimen of biuret.

(ii). The above technique was repeated using dicyandiamide (5 g.). Test portions of the sulphuric acid solution gave positive reactions showing the presence of guanylurea when tested with copper sulphate (characteristic salmon pink precipitate) and with nickel chloride (characteristic yellow precipitate). After neutralising the main solution with barium carbonate the guanylurea was isolated via its copper salt, which was decomposed by hydrogen sulphide. The precipitated copper sulphide was removed, and the filtrate was evaporated to crystallisation point under reduced pressure. Weight of crystalline material obtained was 4.8 g., equivalent to 76 per cent. of the theoretical. After recrystallisation from ethyl alcohol M.P. 104°C.

Action of Heat on Guanylurea Hydrochloride. Finely-powdered, guanylurea hydrochloride (10 g.) was spread in a thin layer in a conical flask heated in an oil-bath. The mass started to melt at 170°C., a strongly exothermic reaction occurred causing sharp rise in temperature, and the fused mass resolidified as the infusible reaction product formed; after 20 minutes heating the reaction was completed. The solid residue was extracted with boiling water to remove ammonium chloride, and then dried. Weight=5.5 g. corresponding to 87 per cent. of the theoretical. The hot filtrate deposited a small amount of microcrystalline solid on cooling, which was identified as ammelide. Found N=44.21 per cent.; $C_3H_4N_4O_2$ requires N=43.75 per cent. The main solid was dissolved in N sodium hydroxide (70 c.c.), filtered from a small amount of insoluble matter, and precipitated by a current of carbon

dioxide gas as a pure white microcrystalline powder. This was filtered off, washed free of sodium bicarbonate, and analysed. Found C=28.30; H=3.96; N=48.98 per cent. $C_2H_3N_3O$ requires C=28.24; H=3.53; N=49.42 per cent. A silver derivative was prepared by adding *N* silver nitrate solution (25 c.c.) to a solution of the compound (2.12 g.) in N potassium hydroxide (30 c.c.). The white precipitate formed was filtered off and dried. Weight=3.8 g. Found Ag=55.81 per cent. $AgC_2H_2N_3O$ requires Ag=56.25 per cent.

Action of heat on an equimolecular mixture of urethane and guanidine carbonate. (i). An intimate mixture of urethane (9 g.) and guanidine carbonate (9 g.) was heated in a conical flask immersed in an oil-bath and fitted with a delivery tube. The evolution of ammonia gas commenced at 70°C., and ethyl alcohol started to distil over at 120°C.; at 130°C. a white sublimate collected in the delivery tube, which proved on examination to be ammonium carbonate. The temperature was maintained at 140°C. for about 60 minutes, by which time all action had ceased. The solid in the flask was extracted with water, in which guanylurea is readily soluble, and filtered. The insoluble residue was dissolved in a dilute solution of sodium hydroxide, and precipitated by carbon dioxide as a white powder, which was filtered off and dried. Weight=6.75 g., corresponding to 75 per cent. of the theoretical. Found N=49.35 per cent.; $C_2H_3N_3O$ requires N=49.42 per cent. The filtrate failed to give the characteristic reddish precipitate of guanylurea upon the addition of copper sulphate and sodium hydroxide solutions.

(ii). A finely-powdered mixture of urethane (4.5 g.) and guanidine carbonate (4.5 g.) was heated as in the previous experiment, but the temperature was not allowed to exceed 110°C. The heating was continued until the evolution of ammonia gas had ceased. The dry residue was recrystallised from ethyl alcohol. Weight=5.6 g., corresponding to 86 per cent. of the theoretical. After drying over sulphuric acid in a vacuum desiccator the M.P. was 118°C. Nencki (14) gives 114°C., and Basterfield and Paynter (15) give 120°C. as the M.P. of guanolin. The identity with guanolin was confirmed by the preparation of the sparingly soluble nitrate. M.P. 181°C. Pinck and Blair (16) give M.P. 182–183°C.

Action of heat on an equimolecular mixture of urea and guanidine carbonate. A mixture of urea (6 g.) and guanidine carbonate (9 g.) was heated as in the previous experiments. At 50°C. the evolution of ammonia gas commenced, and the mass began to fuse at 110°C. The temperature was maintained constant at 130°C. while a brisk effervescence occurred and a sublimate of ammonia carbonate collected in the cold receiver. After one hour the evolution of ammonia gas ceased, and the heating was discontinued. The solid residue was dissolved in dilute sodium hydroxide solution, precipitated by a current of carbon dioxide gas, filtered off, and dried. Weight=8.0 g., corresponding to 94 per cent. of the theoretical. Found N=49.65 per cent. $C_2H_3N_3O$ requires N=49.42 per cent. Silver salt prepared and analysed. Found Ag=57.00 per cent. $AgC_2H_2N_3O$ requires Ag=56.25 per cent.

Formation of Salts with Acids. (i) Nitrate. The copolymer dissolved in concentrated nitric acid on gentle warming, and after the addition of a small amount (ca. 10%) of water the nitrate separated on cooling in the form of small rectangular prisms. On heating the compound decomposed with the evolution of brown fumes at 202°C. without melting. On titration the salt (0.192 g.) required for neutralisation 13.26 c.c. of *N*/10 sodium hydroxide. $C_2H_3N_3O.HNO_3$ would require 13.0 c.c.

(ii) *Sulphate.* The copolymer is dissolved in cold concentrated sulphuric acid, and an equal volume of ice-cold water is added. The clear solution slowly deposited the sulphate in the form of spheroidal granules. On titration the salt (0.158 g.) required for neutralisation 8.00 c.c. of N/10 sodium hydroxide, corresponding to the formula $(C_2H_3N_3O)_2.H_2SO_4.7H_2O$. This formula was confirmed by drying the salt in a vacuum desiccator. Loss in weight=31.5 per cent., the heptahydrate would require a loss in weight=31.99 per cent.

(iii) *Hydrochloride.* The copolymer dissolved on warming in concentrated hydrochloric acid diluted with an equal volume of water, and on cooling the hydrochloride salt separated as a flocculent microcrystalline precipitate. On titration the salt (0.079 g.) required for neutralisation 6.80 c.c. of *N*/10 sodium hydroxide. $C_2H_3N_3O.HCl$ would require 6.50 c.c.

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No. 23.

STUDY OF THE POLYMERISATION OF CYANIC ACID, WITH SPECIAL REFERENCE TO DICYANIC ACID.

By

A. E. A. WERNER AND J. GRAY.

[Read March 25, Published separately July 10th, 1947].

Senier and Walsh (1) showed that when liquid cyanic acid underwent polymerisation at 0°C. the resultant white solid consisted of a mixture of two polymers, namely cyanuric acid and cyamelide, the former being present to the extent of 70 per cent. Later Werner (E. A.) and Fearon (2) studied the polymerisation of cyanic acid at temperatures ranging from 0°C. to 20°C., and found that the proportion of cyamelide in the polymer mixture was greater the lower the temperature. This observation has now been extended to lower temperatures, and, as shown in Table 1, the yield of cyamelide can be increased to almost 70 per cent. by carrying out the polymerisation at —20°C.

Table 1. The Polymerisation of Cyanic Acid.

Temperature of Polymerisation	Weight of Polymeride	Cyanuric Acid Found	Percentage Composition of Polymeride	
			Cyamelide	Cyanuric Acid
0°C.	0.541 g.	0.218 g.	59.6	40.4
	0.532 g.	0.219 g.	58.8	41.2
—10°C.	0.562 g.	0.213 g.	62.1	37.9
	0.550 g.	0.202 g.	63.2	36.8
—15°C.	0.609 g.	0.206 g.	66.1	33.9
	0.652 g.	0.223 g.	65.8	34.2
—20°C.	0.448 g.	0.135 g.	69.8	30.2

Cyamelide is also produced in good yield when a well-cooled suspension of cyanic acid is acidified with dilute hydrochloric acid.

The results tabulated above provide further support for the theory of polymerisation of cyanic acid advanced by Werner (E. A.) (3), who postulated that cyanic acid exists as a keto-enol equilibrium mixture :—

$$H-O-C\equiv N \underset{\text{fall in temperature}}{\overset{\text{rise in temperature}}{\rightleftharpoons}} HN=C=O.$$

Cyamelide is formed by the polymerisation of the low temperature enol form, whereas cyanuric acid results from polymerisation of the keto form. Hence the relative proportions of the two polymerides formed reveal the composition of the equilibrium mixture at any particular temperature.

Owing to the formal analogy between the chemical formula of cyanic acid, $HN=C=O \rightleftharpoons HO-C\equiv N$, and that of cynanamide, $HN=C=NH \rightleftharpoons H_2N-C\equiv N$, attempts have been made to prepare a dimeric form of cyanic acid which would bear the same relationship to the dimeric dicyandiamide as the trimeric cyanuric acid does to the trimeric melamine. Ponsgen (4) originally claimed to have obtained a ' dicyanic acid ', but it was shown by Hallwachs (5) that the substance was merely impure cyanuric acid. Schmidt (6) also claimed to have obtained a small amount of ' dicyanic acid ' by the action of excess phosgene on triuret, but the evidence presented by Schmidt (*loc. cit.*) was very inadequate, and he relied chiefly on the isolation of a silver salt, the analysis of which approximated to that required by the formula $Ag.C_2HN_2O_2$.

There were no further references in the literature to the existence of ' dicyanic acid ' until Davis and Blanchard (7) produced evidence purporting to show that cyanic acid in aqueous and in alcoholic solution dimerises (in part at least) to form a ' dicyanic acid ' according to the following equation :—

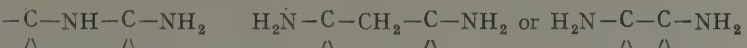
$$H=N-C=O + H=N=C=O \longrightarrow H_2N-CO-N=C=O.$$

Davis and Blanchard (*loc. cit.*) did not succeed in isolating this ' dicyanic acid ', but claimed to recognise its existence in solution by the fact that the well-known biuret reaction was given by solutions which apparently did not contain any actual biuret, since they were unable to isolate biuret from the solid residue remaining after evaporating these solutions to dryness. The pseudo-biuret reaction was assumed to indicate the presence of ' dicyanic acid ', which they failed to isolate because it was completely hydrolysed during the evaporation.

In view of the rather unsatisfactory nature of the experimental evidence adduced in support of the existence of ' dicyanic acid ', to which moreover Davis and Blanchard (*loc. cit.*) have assigned an important role as an intermediate in the formation of allophanates from alcohols and cyanic acid, the present authors have carefully repeated the experiments described by Davis and Blanchard (*loc. cit.*). Our results, however, do not substantiate their claim to have demonstrated the existence of the postulated ' dicyanic acid ' in solution. The positive biuret reaction given by an aqueous solution of cyanic acid, prepared by acidifying sodium or potassium cyanate with the required amount of acetic or hydrochloric acids, was in all cases traced to the presence of biuret, which could in every case be isolated

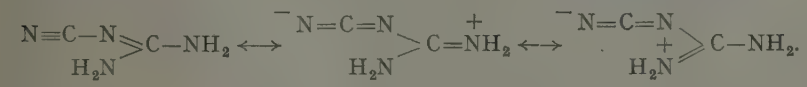
from the solution upon evaporation. Davis and Blanchard (*loc. cit.*) also claimed that ' dicyanic acid ' was formed in the decomposition of both nitrourea and nitrobiuret, but we have found that the positive biuret reaction which developed when an aqueous solution of either nitrourea or nitrobiuret was heated until effervescence commenced was due to the actual presence of biuret. In no case was there ever any indication that a positive biuret reaction was due to any substance other than biuret itself. The formation of biuret under the above experimental conditions is, moreover, to be expected, and its formation is readily explained by the mechanism suggested by Werner (E. A.) and Fearon (*loc. cit.*).

It must also be pointed out that it is extremely doubtful if a substance having the structure postulated for ' dicyanic acid ' would be expected to give a positive biuret reaction. Extensive investigations by Schiff (8) on the constitution of the complex responsible for the positive biuret reaction have shown that only those substances give a positive reaction which possess one of the following groupings in the molecule :—



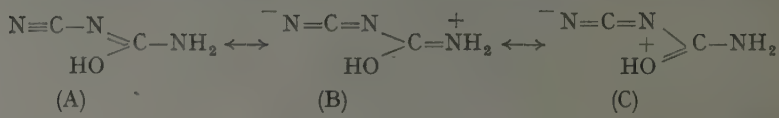
Typical representatives of the three classes are biuret itself, malonamide, and oxamide. The capacity to form a five- or six-membered chelate ring is an essential criterion for a positive biuret reaction. It is clear that ' dicyanic acid ' does not conform to the necessary requirements. Furthermore it has been shown by Jesserer (9) that a refinement of the biuret reaction is possible which permits one to distinguish between the colour reaction obtained with biuret and its immediate derivatives and that given by the compounds belonging to the malonamide and the oxamide classes. The violet copper biuret complex consists of a red and a blue component ; the former is produced alone upon the addition of the first few drops of a dilute copper sulphate solution, giving a characteristic *rose-red* colour, which only changes to the usual *violet* colour upon the addition of a further quantity of copper sulphate solution. In all our experiments this characteristic colour sequence was observed when testing for biuret. This affords additional proof that the biuret reaction observed in our experiments was due to the presence of biuret, and not ' dicyanic acid '.

It is finally of interest to discuss possible reasons why ' dicyanic acid ' is not a stable substance, particularly in view of the established existence of *dicyandiamide*, the dimer of cyanamide, and Hallwachs' acid or *cyanurea*, a codimer of cyanic acid and cyanamide. The cyanguanidine structure for dicyandiamide has recently been definitely established as the result of an X-ray crystallographic analysis by Hughes (10), who showed that it exists as a resonance hybrid of the structures :—

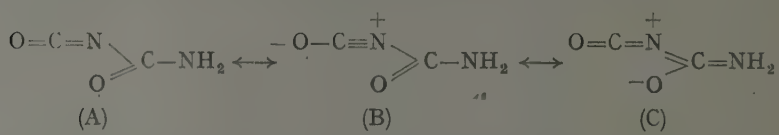


Since all three structures contribute almost equally to the resonance hybrid, the resonance energy of the dicyandiamide molecule is large, and undoubtedly is responsible for the relative stability of dicyandiamide. The cyanurea structure for Hallwachs' acid has not yet been investigated by the X-ray crystallographic technique, but there is a considerable amount of chemical evidence (as shown in the preceding

communication) in support of such a structure for Hallwachs' acid. On the basis of such a cyanurea structure the positions of the atoms would correspond to a molecule, which may be represented as a resonance hybrid, involving mainly the structures (A) and (B) but with a smaller contribution from the structure (C).



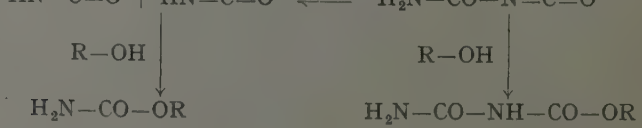
In this case the resonance is not so complete, the resonance energy is consequently smaller, and the compound will be less stable than dicyandiamide (as is actually the case) but still sufficiently stable to be easily isolated and withstand heating in aqueous solution up to a temperature of 80°C. However in the case of ' dicyanic acid ' a similar type of resonance is impossible ; the contribution of the postulated components (B) and (C) of the possible resonance system shown below :—



will be almost negligible—hence there will be no gain in stability due to resonance energy, and ' dicyanic acid ' may therefore be expected to be less stable than either dicyandiamide or Hallwachs' acid.

Another point of interest, which is apposite to the present discussion, is the existence of thiodicyanic acid, $H_2N{-}CO{-}N{=}C{=}S$, obtained recently by Birckenbach (11) in good yield by the condensation in ethereal solution at 0°C. of equimolecular amounts of cyanic and thiocyanic acids. This compound can be heated up to 105°C. before undergoing decomposition, but is *instantly hydrolysed in the presence of traces of moisture.* Now it is a well-known fact that the thio derivatives of carbamic acid are more stable than their oxygen analogues, and therefore the fact that thiodicyanic acid is so readily hydrolysed by traces of water is strong evidence against the possible existence of ' dicyanic acid ' under the experimental conditions described by Davis and Blanchard (*loc. cit.*), and until further evidence is forthcoming the existence of ' dicyanic acid ' must be regarded as extremely doubtful.

In view of the probable non-existence of ' dicyanic acid ' it is now necessary to reconsider the claim advanced by Davis and Blanchard (*loc. cit.*) that when an aqueous solution of cyanic acid reacts with alcohols not only carbamates but also allophanates are formed, both however in small yields. The formation of the allophanates is ascribed by these authors to the presence of ' dicyanic acid ' as an intermediate, and the series of reactions was represented as follows :—



We have repeated the experiments of Davis and Blanchard (*loc. cit.*), but were only able to isolate ethyl allophanate in very small yield when the reaction was carried out in 50 per cent. alcohol water mixture, and hydrochloric acid was present in slight excess. We found, moreover, that, if an excess of hydrochloric acid is avoided, the sole product of the reaction, in either absolute alcohol (which ought to be a better medium for 'dicyanic acid') or a 50 per cent. alcohol water mixture, was the carbamate. Ethyl allophanate was only produced in a reasonable yield when the reaction was carried out in absolute alcohol and hydrochloric acid was present in excess. These results are in agreement with the general mechanism presented by the authors in a previous communication (12), in which they showed that cyanic acid could combine with carbamates only in the presence of hydrochloric acid. It thus follows that the formation of allophanates is due to the addition of cyanic acid to the carbamate molecule, and does not proceed as the result of the union of an alcohol with the hypothetical 'dicyanic acid'.

EXPERIMENTAL.

Polymerisation of cyanic acid at low temperatures. Samples of liquid cyanic acid, prepared by the thermal decomposition of anhydrous cyanuric acid at dull red heat, were confined in thin layers in narrow thin-walled tubes immersed in baths maintained at 0°C. (ice and water), −10°C. (ice and salt), −15°C. and −20°C. (ice and calcium chloride in suitable proportions), respectively. This technique ensures a fairly accurate control of the temperature, and by efficient dissipation of the heat of polymerisation reduces to a minimum any tendency for the temperature to rise. When polymerisation was completed, a weighed quantity of the polymeride was extracted with hot water, and, after removal of the insoluble cyamelide, the cyanuric acid in solution was determined by titration with $N/10$ sodium hydroxide using phenolphthalein as indicator.

Cyanic acid in absolute ethyl alcohol solution. (a) Sodium cyanate (6.5 g.) was added in portions to $2N$ solution of hydrochloric acid in absolute ethyl alcohol (50 c.c.) maintained at about 10°C. The reaction mixture was left overnight, and then filtered to remove the insoluble sodium chloride. The alcoholic filtrate was concentrated in a vacuum desiccator over sulphuric acid, and the crystalline material which collected was dried and weighed. Weight=5.00 g., corresponding to 60 per cent. of the theoretical. M.P. 48°C., not depressed by admixture with an authentic specimen of ethyl carbamate. (b) Sodium cyanate (6.5 g.) was added in portions to a solution of hydrochloric acid in ethyl alcohol, and simultaneously a current of dry hydrochloric acid gas was passed, while the temperature was kept at about 10°C. by external cooling. After all the sodium cyanate had been added the reaction mixture was left overnight, and then filtered. The dried solid residue was extracted with boiling benzene, and yielded ethyl allophanate, M.P. 193°C., not depressed by admixture with an authentic specimen. Weight 4.2 g., corresponding to 64 per cent. of the theoretical. On concentration *in vacuo* the alcoholic filtrate yielded ethyl carbamate. M.P. 48°C. Weight=1.5 g.

Cyanic acid in aqueous alcoholic solution. Ethyl alcohol (30 c.c.) was added to a solution of potassium cyanate (16.2 g.) in distilled water (30 c.c.). The solution

was acidified with hydrochloric acid, allowed to stand at room temperature one hour, and then evaporated to dryness. Extraction of the solid residue (Wt.=20 g.) with ether gave urethane. M.P. 48°C. Weight=0.40 g. corresponding to 2.3% of the theoretical. Extraction with boiling benzene yielded ethyl allophanate. M.P. 192°C. Weight 0.24 g. corresponding to 1.8% of the theoretical. The solid residue contained ammonium chloride. Wt.=5.5 g., corresponding to 50 per cent. of the theoretical derived from the hydrolysis of cyanic acid.

Formation of biuret in aqueous solutions of cyanic acid. (a) Glacial acetic acid (6 c.c.) was added slowly to a well-stirred solution of potassium cyanate (8.1 g.) in water (20 c.c.). After neutralisation with sodium carbonate the solution gave the characteristic biuret reaction. The solution was evaporated to dryness on a water-bath, and the residue also gave a positive biuret reaction. This residue was extracted with a hot solution of potassium hydroxide to dissolve out the biuret. The alcoholic solution was acidified with hydrochloric acid, and after removal of the precipitated potassium chloride the filtrate gave a strong positive biuret reaction, and yielded a residue of impure biuret. Recrystallised from alcohol. M.P. 188°C. not depressed by admixture with an authentic specimen of biuret. (b) Concentrated hydrochloric acid (10 c.c.) was slowly added to a well-cooled (−10°C.) suspension of sodium cyanate (6.5 g.) in distilled water (50 c.c.). A fine precipitate formed, and a strong odour of cyanic acid developed. After standing for one hour the solution was filtered. The residue proved to be cyamelide admixed with cyanuric acid, identified by means of its characteristic violet copper ammonium salt, and the filtrate gave a strong positive biuret reaction. On evaporating the filtrate to dryness and subsequent extraction with alcoholic potassium hydroxide biuret was isolated and identified by a mixed M.P. with an authentic specimen of biuret.

Decomposition of nitrourea in aqueous solution. A solution of nitrourea (2.0 g.) in water (20 c.c.) was slowly evaporated to dryness on a water-bath during which effervescence occurred. The residue gave a positive biuret reaction, and a sample of biuret was isolated. M.P. 188°C. not depressed by admixture with an authentic specimen of biuret.

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No. 24.

NOTES ON THE ACIDITY, CHLORIDE CONTENT, AND OTHER CHEMICAL FEATURES OF SOME IRISH FRESH WATERS.

By

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Ireland is a country rich in rivers and lakes, but comparatively little is known of the chemistry of its fresh waters. The observations in this field that are here reported have been made from the standpoint of the hydrobiologist. No complete analyses are presented, but attention has been focussed on certain constituents that are likely to be of biological importance. Some of the findings possess, however, a certain geochemical interest.

Part of the expenses incurred in these investigations were defrayed by a grant from the Society for this purpose.

pH.

Of all the chemical factors that govern the distribution of fresh-water organisms *p*H is probably the most important. It is well known, for example, that the majority of animals with a calcareous exoskeleton are unable to tolerate strongly acid waters ; while in the plant kingdom a large number of aquatic, as of terrestrial species, are restricted to a certain range of *p*H in their environment.

Many fresh waters, especially those that are neutral or slightly acid, possess such a low buffer capacity that certain precautions must be observed if accurate determinations of *p*H are to be obtained. The determinations reported in this paper were all made on the spot, so that errors arising from change of acidity during transport or storage were eliminated. But all colorimetric determinations of weakly buffered solutions are subject to the possibility of error arising from the change of *p*H produced by the addition of the indicator itself, which, being the salt of a weak acid, may in an unfavourable case exert a greater influence on the final value of the *p*H than do all the original constituents of the water. Although this danger has several times been pointed out, the fact that figures are often published which appear to rest on a single colorimetric reading shows that it is not as widely appreciated as it should be.

There are several ways in which the disturbing influence of the indicator on the *p*H may be either discounted or eliminated. That which I have adopted is very simple, and is based on a method described by Clark (1920). Several distinct solutions of each indicator are made up, one with the normal quantity of alkali added (sufficient

for half neutralization), and the others with slightly differing quantities. The *p*H of each of these indicator solutions is then determined. This may be most conveniently done by using a Duboscq colorimeter to match a very small depth of the indicator solution against either a deeper layer of the indicator in a buffer solution of known *p*H or else a standard glass of a Lovibond Tintometer. In this way four solutions of bromothymol blue, for example, will be made up, with their *p*H at 6.2, 6.5, 6.8, and 7.2. When a similar series has been made up for the other indicators in use it is possible to ensure that the final determination of the *p*H of a water is always made with an indicator solution of which the *p*H is very close to that of the water that is being tested. Let us suppose that the first test is made with the bromothymol blue solution that is made up to *p*H 6.2, and that the colour so obtained corresponds to *p*H 6.45. The next test is made with indicator made up to *p*H 6.5, and this gives, let us say, a reading of 6.6. Next the bottle of *p*H 6.8 is used, and the reading is 6.7. It is clear from the last two results that the true *p*H of the water must certainly lie between 6.6 and 6.7. By a series of successive approximations of this kind, which is carried on until, of two indicator solutions whose own *p*H values differ by 0.4 or less, one shows a reading lower than its own *p*H value and the other higher, it is possible to obtain reliable determinations, with an error of not more than 0.1, of the *p*H of even the most feebly buffered natural waters.

The determinations were made with a Lovibond Tintometer, which is a simple comparator fitted with standard coloured glasses which correspond to nine tints within the working range of each indicator. The indicators used were bromocresol green, chlorophenol red, bromothymol blue, phenol red and thymol blue.

By means of this technique about 250 readings have been taken of the *p*H of Irish fresh waters. The following are the main conclusions that can be drawn from the results.

(1) The range of *p*H of natural waters in Ireland is from 4.1 to 8.75.

(2) Waters derived from a catchment area that is wholly or largely limestone have a *p*H that is always above 7.5 and usually above 8, and are well buffered. The *p*H of water that has been in effective contact with limestone for any length of time is always close to 8.5. The alkali reserve of a limestone water is sufficient to neutralize a large amount of humus acids. This is well illustrated by such rivers as the Inny (Co. Westmeath), which draws most of its waters from the large raised bogs of northern Westmeath, but includes also in its catchment area some grassland lying on limestone drift. At Float Bridge (just above L. Derravaragh) its water, though very brown, is alkaline, with a *p*H varying from 7.55 to 8.15. In L. Derravaragh itself, the shores of which are almost entirely limestone, the *p*H of the same water becomes raised to 8.4 and the colour is discharged, presumably by precipitation of colloidal humic compounds.

Some other determinations for limestone waters are :—

	*p*H		*p*H
L. Gill	8.2 ; 8.65	Brittas R., Co. Wicklow	8.35
L. Cuilin, Co. Mayo	8.4 ; 8.55	L. Corrib	8.3 ; 8.4
L. Gara, Co. Sligo	8.65 ; 8.25	L. Mask	8.3
L. Key, Co. Roscommon	8.7	L. Derg, at Killaloe	8.4
L. Arrow, Co. Sligo	8.45	L. Leane (E. shore)	8.45
R. Boyne, at Trim	8.1		

In this table, as in others, when two figures are quoted for the same water it is to be understood that different readings were obtained on two different occasions.

The highest *p*H value that I have met with in any substantial body of water is 8.75, which is recorded for L. Labe, a small lake in S.E. Co. Sligo, derived from underground drainage of limestone mountains. Its effluent stream vanishes after about a mile in a swamp in which constant precipitation of calcium carbonate is taking place.

Waters draining off basalt are also distinctly alkaline, though usually rather less strongly buffered than those from limestone. For example the stream in Glenariff, Co. Antrim, despite the fact that most of its catchment area is peat-covered, has, even at about 900 ft., a *p*H of 8.25. Similar figures have been recorded for other streams on the Antrim basalt.

(3) Distinctly acid waters are not nearly as widespread as is commonly supposed, and *p*H values lower than 5 are to be found only in water that has drained off a substantial mass of peat. I cannot agree with Southern (1932) when he says: "The most acid kind of water is found in lakes which have very limited catchment basins consisting of steep slopes of non-limestone rock." Only two such lakes (Nahanagan and Acorrymore) have I found to be acid at all (and those not very strongly); many others that I have tested are virtually neutral. Pure peat-water, *i.e.* the contents of bog-holes, bog-drains, and slow streams running through large bogs, has a *p*H that is always close to 4.4, but as the following table shows, the figures for Connemara are higher than those for Co. Wicklow, and those for Kerry are higher still.

Source of R. Liffey, Co. Wicklow	4.1; 4.25
Two Rock Mountain, Co. Dublin	4.2
Bog pool near Maam Cross, Co. Galway	4.5
,, ,, ,, Recess ,, ,, ...	4.45
,, ,, ,, Craiggamore ,, ,, ...	4.35
Bog N.E. of Brandon Mt., Co. Kerry	4.55
Bog at 1,000 ft. on W. slope of Carantuohill	5.1
Bog-pool in Glencar, Co. Kerry	4.95
Peat 2 ft. below surface of bog near Upper Lake, Killarney	5.0

These figures agree with those reported by Pearsall (1938) for the *p*H of peat samples; he found that the average value in the Connemara blanket bog was about 4.5, which contrasts sharply with the much greater acidity (down to *p*H 3) characteristic of the blanket bog of Northern England. The difference is ascribed by Pearsall to the wetter summers in Ireland, which prevent temporary drying-out, with consequent oxidation. Why the peat of Kerry should be less acid still is not yet apparent.

All the samples of acid waters so far cited have been those that are in contact solely with peat. Water flowing or resting on a rocky substratum is never quite so acid, but a number of *p*H values between 4.6 and 5.6 have been met with in mountain streams and tarns. For example:—

Upper L. Bray, Co. Wicklow	4.75
Effluent from Lower L. Bray	4.65; 4.9
L. Nahanagan, Co. Wicklow	5.05; 5.5
L. Acorrymore, Achill Island	5.55
Glenmacnass R., Co. Wicklow	4.7; 5.0

Several more examples from Co. Wicklow could be given, but it is remarkable that this relatively high figure of 5.55 is the lowest *p*H that I have found for any lake in Western Ireland. (By "lake" is implied water resting in a rocky basin, and not a mere bog-hole.)

(4) In a very large proportion of the lakes and rivers of non-calcareous areas (which includes, of course, most of the mountain districts) the water is very faintly acid, neutral, or even slightly alkaline; *i.e.* its *p*H ranges from 6.0 to 7.3. As the existence of this large class of quasi-neutral waters does not seem to be generally realized, it is worth while quoting a fairly extensive list of measurements.

Co. Cork

Owvane R., Bantry Bay	6.9
Gouganebarra L.	7.1
Largest stream entering Gouganebarra L.	6.8
Bandon R., near Dunmanaway	7.15

Co. Tipperary

Bay L. (Knockmealdowns)	6.4; 7.0

Co. Galway

L. Mask, S.W. limb .. .	6.9
L. Fee	6.9
L. Nafooey	6.95
L. Inagh	7.1; 7.2
L. Derryclare	7.0; 7.05
L. Nabrucka	7.1
L. Oorid	7.15
Glendollagh	7.05
L. Nacoogarow	7.1
Ballynahinch L.	7.0
,, R.	6.95
Craiggamore L.	6.7
Owentooey R., Recess (in spate)	6.3
Stream on N. side of Leckavrea Mt.	6.95

Co. Kerry

Owenshagh R., Lauragh	6.2
Glanmore R., Lauragh	6.85
L. Acoose	7.15
L. Coumloughra	7.2
Caragh R., above Lough	6.25
Caragh L.	6.75
Stream from main corrie of Brandon Mt.	6.85
Curraheen R., Slieve Mish Mts., at 700 ft.	6.9

Co. Mayo

Doolough	6.9; 7.05; 7.15
Carrowhisky R.	6.75
Owenmore R., Bangor	6.7
Stream on Benwee Head	7.1

Co. Waterford

Coomshingaun L.	7.05
Stream from plateau above Coomshingaun	6.8

Co. Wicklow

Stream on E. side of Djouce	6.5
Glendasan R., Laragh	6.45
Glendalough, upper lake	6.25

A few of the waters in this list, such as those of Gouganebarra, Coomloughra, Doolough and Coomshingaun, are from lakes of which the catchment area is mainly steep mountainsides on which little or no peat is developed, and their neutrality is therefore not very surprising. But the great majority run off an area that is largely or at any rate partly peat-covered, and it must be concluded that the original acidity of the water is lost. The constancy with which the Connemara lakes, in particular, maintain a *p*H within 0.2 units of neutrality is very striking, and affords a partial explanation of the anomalies in their flora that have puzzled ecologists, such as the frequent occurrence of *Cladium mariscus*, a characteristic fen species.

These same neutral lakes, resting in granite, quartzite, or mica-schist basins, are surrounded by blanket bog, from which acid water of *p*H about 4.4 drains constantly into them. It would seem, therefore, that the acid must be neutralized, or precipitated, or chemically destroyed when the water flows into the lake basin and loses contact with the peat.

If it is neutralized there are two possible sources for the necessary base : veins and dykes of metamorphic limestone, intrusive basic rocks, etc., in the lake basin, or blown sand rich in calcareous debris. The latter explanation has been rather freely invoked by botanists, but I do not believe that it applies to any but a very few small lakes that are within a mile or so of extensive sandy shores. It can, in any case, be shown that the water of these Connemara lakes has a total base content that is very little higher than that of the acid bog-water which drains into them, and therefore that the loss of acidity is not principally due to neutralization by bases from whatever source. This may most easily be done by determining the weight of sulphated ash that remains after evaporation and ignition in presence of sulphuric acid. The following figures were obtained :—

	Sulphated ash, mg. per litre	*p*H
L. Nacoogarrow	65.4	7.1
Adjacent bog-pools (mean of two)	62.1	4.45

The difference, which is scarcely significant, implies the addition of only about 0.05 milli-equivalents of base per litre, which could not, in itself, account for the rise in *p*H.

It would seem therefore that the organic acids of the peat-water must be either precipitated or destroyed (by oxidation or otherwise) in the lake-basin. The fact that these lakes have, for the most part, clean rocky bottoms, without any appreciable deposit of organic mud, renders the first alternative unlikely ; but the question clearly requires further investigation.

Attention may be drawn to the fact that in the Co. Wicklow waters examined the loss of acidity does not proceed quite so far. This is possibly connected with the greater acidity of the peat in Eastern Ireland, which has been mentioned above.

An important feature of quasi-neutral waters of this type is their extremely low buffer capacity, which is due to the virtual absence of weak acids other than carbon dioxide. Accurate determination of their *p*H requires, accordingly, some care. A remarkable illustration of this low buffer capacity was met with in Gouganebarra L. (Co. Cork), a mountain tarn of which the catchment area consists entirely of Old Red Sandstone. My first test gave me the astonishing figure of *p*H 9.0. Another sample from 200 yards along the shore showed *p*H 8.7. Eventually I found that this alkaline water was confined to one corner of the lake, and that the *p*H all along the further shore was constant at 7.1. The alkalinity must have been due to contamination from the small hotel which stands on the lake shore near my first point of sampling, and which was, presumably, discharging washing soda into the lake. This had been sufficient to raise by nearly 2 units the *p*H of some acres of water.

Waters of this type, which include the greater part of the mountain lakes and rivers of Ireland, are essentially dilute solutions of neutral salts, containing a quantity

of carbon dioxide determined by the partial pressure in the atmosphere, and a very minute amount of excess base, which must be derived either from solution from the soil, or from blown dust, or from adsorption of acid radicles. Sawyer (1944) has shown that many of the fresh-water lochs of Sutherlandshire are of this type, and owe their slight acidity (*p*H *circa* 6.1) entirely to carbon dioxide.

(5) There are, of course, neutral or nearly neutral waters of another type: those derived from the mixture of acid and alkaline streams, or by acid water running for a short distance over a calcareous substratum. They are, in contrast to the waters of the previous type, relatively well buffered. The R. Inny, above L. Derravaragh (mentioned earlier) belongs here, as does the middle course of the R. Liffey, in and above the new reservoir, and the middle course of most Irish rivers. A few other examples are:—

L. Graney, Co. Clare	7.4
L. Levally, Co. Mayo	7.8
L. Beltra, Co. Mayo	7.45
R. Rinn, Co. Longford	7.35
Stream in Glendoo, Co. Dublin	6.6
R. Blackwater, Co. Cork (above Banteer)	7.3

The occasional occurrence (as in Glendoo) of waters of this type in streams running off mountains of siliceous rock is due, of course, to the presence of calcareous glacial drift in some part of their catchment area.

(6) If water flowing from a limestone area lies in a non-limestone basin, or if a river flows successively through the two types of rock, the effect of the limestone is, as a rule predominant. The case of the R. Inny has been mentioned earlier. The reverse phenomenon is seen in L. Cuilin, Co. Mayo, which lies entirely on granite. Its water, however, being derived mainly from the limestone country of E. Mayo, has a *p*H of about 8.5, and the figure is not perceptibly lowered by its sojourn in the granite basin.* Neutral waters, on the other hand, need to flow over limestone for only a very short distance to become distinctly alkaline. The stream which flows from the Curlew Mts. into the S.W. corner of L. Arrow (Co. Sligo) rises on Old Red Sandstone. At the point where it reaches the limestone its *p*H is 7.2. 300 yards lower down it has risen to 7.75; after a further 300 yards to 8.2; and finally, on entering the lake after about 1½ miles on limestone, to 8.4. In other cases the joint result of inflow of tributaries and solution of the river-bed is to bring about much more complex gradients, as in the lower reaches of the R. Flesk (Co. Kerry) which runs through sandstone drift over limestone, and varies in its *p*H in the most irregular manner from 7.3 to 8.6 in the last four miles of its course.

(7) Variation of *p*H with season and weather is less common and less extensive than one might suppose. Flooding always lowers the *p*H, by increasing the amount of humus in suspension and also perhaps, in alkaline waters, by simple dilution. Frost (1939) has published figures for the Liffey, and finds that the water at Ballysmuttan varies in *p*H from 4.6 to 6.8, with an average of 5.6. My own determinations at the same station confirm this range of variation, but I believe it to be exceptionally

* It is, however, interesting to note that *Lobelia dortmanna*, a plant distinctly calcifuge in its distribution, grows freely in L. Cuilin and the S. part of L. Conn, but not along the limestone shores of northern L. Conn. The possibility of a *p*H gradient in the subaqueous soils of such lakes must be born in mind.

wide, and likely to occur only in places where very acid water, like that of the upper Liffey, is changing over a short distance to alkaline, probably by the combined effects of oxidation and neutralization by calcium carbonate. Most of the other waters which I have sampled at different seasons show a range of 0.4 units or less, and some of the western lakes (e.g. Doolough) show a constancy that is especially remarkable if their low buffer capacity is taken into consideration. Even rivers can show the same constancy: the Caragh River, for example, just above the lake, sampled in July at normal summer level showed a *p*H of 6.2; two days later, in raging flood after a day's continuous rain, the value had risen only to 6.3.

Titratable Acidity and Alkalinity.

Although *p*H is, in general, the most useful measure of acidity for the hydrobiologist, the titratable values of acidity and alkalinity are of some interest to the hydrographer and chemist. They enable one to distinguish between different buffer capacities in waters of the same *p*H, and to make, in some instances, deductions as to the nature of the acids and bases present.

In making these titrations I have somewhat modified the standard methods of water analysis. For determination of titratable *acidity* the water is titrated against *N*/200 sodium hydroxide with phenol red as indicator and an end-point at *p*H 7.5. In this way the carbon dioxide originally present in the sample is taken into account (*i.e.* it is neutralized as far as $NaHCO_3$), but re-equilibration with the atmosphere does not take place to any appreciable extent. To ensure this the titration is carried out reasonably quickly; but since the reaction $CO_2 + H_2O \longrightarrow H_2CO_3$ is a slow one, 3–5 minutes should be allowed at the end of the titration before the end-point is finally judged. For determinations of titratable *alkalinity*, it is best to determine the excess base, irrespective of the extent to which it is combined with carbonic acid. This is done by titrating against *N*/200 HCl to an end-point at *p*H 5.5, using chlorophenol red as indicator. Since, during the titration, the liquid becomes supersaturated with carbon dioxide released by the added acid, it is brought to the boil shortly before the end-point, cooled, and the titration completed in a solution which is now virtually free from carbon dioxide.

The following table shows some of the values that have been obtained, the concentrations being expressed in milli-equivalents per litre.

Source of water	*p*H	Acidity (mEq./l.)	Alkalinity (mEq./l.)
L. Bray, Co. Wicklow	4.6	0.13	—
Bog pool on Two Rock Mt., Co. Dublin	4.2	0.32	—
Source of R. Liffey, Co. Wicklow	4.1	0.47	—
L. Nahanagan, Co. Wicklow	5.5	0.035	—
Stream on Tonelagee, Co. Wicklow	4.7	0.09	—
L. Acorrymore, Achill Island	5.55	0.115	—
Doolough, Co Mayo	7.05	0.07	0.26
L. Fee, Co. Galway	6.9	0.06	0.085

(*continued overleaf.*)

Source of water	*p*H	Acidity (mEq./l.)	Alkalinity (mEq./l.)
Stream on Leckavrea, Co. Galway	6.9	—	0.34
Stream on Benwee Head, Co. Mayo	7.05	0.06	0.64
Stream in Glenariff, Co. Antrim	8.25	—	2.14
L. Derravaragh, Co. Westmeath	8.4	—	3.64
R. Inny, above L. Derravaragh	7.55	—	3.20
L. Cuilin, Co. Mayo	8.55	—	1.88
L. Gill	8.2	—	1.16

It will be seen that the figures for alkalinity are, in general, much higher than those for acidity, the concentration of acid even in the exceptionally acid and very dark brown sample from the source of the Liffey being less than $N/2000$. For as weak a solution as this to show a *p*H as low as 4.1 implies that part of the acid in solution must be relatively strong, that is to say of at least the strength of acetic acid; and the same is true, to a greater or less extent, of all the acid waters investigated. In the hopes of throwing further light on this point titration curves were prepared for the first two waters listed above: these curves are reproduced in the figure. The absence of any well-marked points of inflection in the curves suggests that at no stage in the titration are we concerned with a single acid, but that in addition to carbon dioxide both weak and relatively strong organic acids are present, the weaker being associated with brown colour, and perhaps colloidal. The divergence between the curves for boiled and for unboiled samples gives, of course, a measure of the part played by carbon dioxide in solution.

In limestone waters the lack of exact correlation between *p*H and titratable alkalinity is due, presumably, to the fact that in some of them the *p*H is lowered by organic acids that have been neutralized, but not precipitated or destroyed. The water of L. Derravaragh, with a very high calcium content (which is virtually a measure of the excess base) still retains in solution some of the acids brought down by the Inny from the peat-bogs, and has therefore a lower *p*H than the water of L. Cuilin, in which dilution of the limestone-water by nearly neutral streams flowing off granite and quartzite considerably lowers the value of the excess base but has little effect on the *p*H.

Sodium and Chloride Content.

The importance to most aquatic animals of the concentration of sodium chloride in the medium in which they live is not yet generally appreciated. All animals, with the possible exception of insects, require a relatively high concentration of sodium chloride in their body fluids, and it has been shown by Krogh and his pupils (for summary see Krogh, 1939) that most fresh-water animals obtain this by absorbing the salt from their environment against a concentration gradient. In many cases this power of absorption is astonishingly highly developed: the crayfish, for example, can absorb the sodium chloride so completely from a 1.1 mM. solution (0.0064%) as to reduce it to a concentration so low that the chloride cannot be detected ($<$0.02 mM.). Similarly the stickleback can absorb sodium chloride from all solutions stronger than 0.25 mM. It would appear that for each species there is a minimum concentration below which absorption cannot be carried on—or rather cannot be carried on faster than the inevitable outward diffusion that is proceeding all the time in the opposite direction.

It would seem probable, therefore, that the sodium chloride content of the water might in some cases be a limiting factor in the distribution of fresh-water animals. A number of analyses of Irish waters have been made to elucidate this point. In particular, special attention was paid to waters derived from catchment basins composed entirely of highly insoluble rocks such as quartzite ; for in these it might be expected that the amount of salts derived from weathering would be infinitesimal.

Since the estimation of chloride presents much fewer analytical difficulties than the estimation of sodium, most of the analyses were made for chloride. The water was first concentrated by evaporation to about a fifteenth of its original volume, and the chloride in the concentrate estimated by the method of Conway (1935) with minor modifications. This consists in oxidizing the chloride quantitatively to chlorine by potassium permanganate and sulphuric acid in the outer chamber of a micro-diffusion unit, and allowing it to distil over into potassium iodide solution in the inner chamber. The iodine released is estimated by titration with $N/500$ sodium thiosulphate.

The figures thus obtained are shown in the following table. (The concentration of chloride is expressed in millimoles per litre : one part of Cl in 100,000=0.285 mM.)

Source	Date	W. Long-itude	Rocks of catchment basin	Cl (mM.)
L. Bray, Co. Wicklow	7/'40	6°20′	Granite	0.165
,, ,, ,, ,, ...	11/'46	,,	,,	0.12
Source of R. Liffey	7/'40	,,	Peat on granite	0.15
Stream in Glendoo, Co. Dublin	4/'45	,,	Granite, with some drift	0.29
Glendalough, Co. Wicklow	5/'45	,,	Mica-schist	0.19
L. Nahanagan, Co. Wicklow	7/'40	,,	Granite	0.135
Stream on Tonelagee, Co. Wicklow	5/'45	,,	,,	0.175
Stream in Glenariff, Co. Antrim	3/'41	6°5′	Basalt	0.29
L. Derravaragh, Co. Westmeath	7/'40	7°20′	Limestone	0.34
R. Inny, above L. Derravaragh	7/'40	7°25′	Limestone, largely peat-covered	0.31
Coumshingaun L., Co. Waterford	3/'46	7°30′	Sandstone	0.37
L. Muskry, Galtee Mts.	6/'45	8°5′	Sandstone	0.26
R. Blackwater, near Banteer, Co. Cork	3/'46	8°55′	Mainly coal measures	0.39
L. Cuilin, Co. Mayo	1/'41	9°10′	Limestone and granite	0.54
Stream on Leckavrea, Co. Galway	1/'41	9°35′	Quartzite	0.48
Doolough, Co. Mayo	8/'41	9°45′	Slates	0.39
L. Nacoogarow, Co. Galway	6/'45	,,	Mica-schist	0.51
Bog near Recess, Co. Galway	6/'45	,,	Peat on mica-schist	0.60
L. Craiggamore, Co. Galway	6/'45	10°	Mica-schist	0.86
L. Acorrymore, Achill I.	7/'40	10°10′	Quartzite	0.60
Stream from coomb on Brandon Mt., Co. Kerry	3/'46	10°10′	Sandstone	0.40

Attention may first be drawn to the relative uniformity of the figures. The greatest concentration of chloride recorded is only seven times the least, a range which in view of the great variety of the sources of water is less than one might expect. Secondly, it will be seen that whereas there is no correlation with the type of rock from which the water flows, there is a general correlation with geographical position, the highest concentrations of chloride being found in waters near the west coast, the lowest in those furthest from it. The samples in this table can be classified as 8 eastern, 4 central, and 9 western, and the average chloride content for these three classes respectively is 0.19, 0.32 and 0.53 mM.

The explanation is simple enough: practically all the chloride in Irish fresh waters is derived from sea spray, and comes down in the rain. Owing to the greater frequency and greater force of westerly, as compared with easterly winds, the rain in western districts is more heavily charged with sea salt.

That there is a considerable transport of salt from sea to land in this fashion has been recognized for some time, but that in countries such as the British Isles, in which no place is very far from the sea, the chloride of fresh waters is derived almost entirely from sea spray and scarcely at all from the soil, has not been very generally realized. This view was long ago urged by Ackroyd (1901); and the fact that some unwarrantable conclusions drawn by Ackroyd in the same paper were successfully refuted by Joly (1901) has perhaps obscured the truth of this part of their foundation. Few figures are available for the chloride content of Irish rain: Ackroyd quotes 47.2 parts Cl per million (1.33 mM.) as the annual average for Valentia, and a recalculation of the data furnished by Leonard *et al.* (1943) shows that the average for Glasnevin (where it is perhaps slightly increased by urban pollution) is 5 parts Cl per million (0.14 mM.). These figures may be compared with 1.0 mM. for Liverpool and 0.115 for Kew (Leonard and McVerry, 1939). It will be seen that when allowance has been made for evaporation the rain chloride alone will provide concentrations at least as high as those indicated in my analyses.

The fact that the correlation in my table between chloride concentration and western situation is not quite exact is due partly to the topographical accidents of the different stations, and partly to variation with weather and season. All published figures for rain show a very wide range of variation in chloride content from one sampling to the next, being highest for light rain in stormy weather and lowest for heavy rain in calm weather; and although this variation is largely averaged out by the mixing that takes place in the soil and in streams, it will not be wholly suppressed. A range of variation such that the maximum chloride content is twice the minimum is probably not unusual for Irish fresh waters.

So far we have considered chloride alone: what about the sodium by which it must be accompanied? Accurate estimation of sodium at a concentration of about 5 parts per million is no easy matter, but I have performed a few analyses by a modification of the method of Barber and Kolthoff (1928). 100 ml. of the water is evaporated to dryness, and the residue, after cautious ignition, taken up in 1 ml. of distilled water. The sodium is precipitated as sodium zinc uranyl acetate, and weighed in the filter-crucible in which precipitation is carried out.

	Na present (mM.)	Na "equivalent" of Cl present (mM.)	Excess Na (mM.)
L. Bray, Co. Wicklow	0.235	0.14	0.095
Source of R. Liffey	0.205	0.13	0.075
L. Nahanagan, Co. Wicklow	0.130	0.115	0.015
L. Acorrymore, Achill I.	0.57	0.515	0.055
Bog-pool at Recess, Co. Galway	0.505	0.515	—0.01
L. Craiggamore, Co. Galway	0.68	0.74	—0.06

The figures in the second column of this table show the sodium equivalent of the chloride present in the water—equivalent not in the chemical sense, but representing the amount of sodium present in the volume of sea water which would be required to provide this amount of chloride. In other words, if it be assumed that all the chloride is derived from sea water, then the concentration of sodium from this source alone is represented by the figures in the second column. It will be seen that there is a fairly close correspondence between these values and the amount of sodium actually present, which indicates that sea spray brought down in the rain is the principal source in Irish fresh waters of this element also. There is, however, in three of the samples a difference between the two figures which is probably significant, and the positive value of these figures for excess sodium indicates that the rain-borne sodium is supplemented by a smaller quantity (about 2 parts per million) which is presumably derived from weathering. In the third and fifth samples the Na/Cl ratio is almost exactly that of sea water, and the figure for excess sodium is practically zero. In the last sample, however, this figure is negative and large enough to make it unlikely, though not impossible, that it arises entirely from analytical errors. The excess of chloride over sodium in this water would imply either that a significant part of the chloride is derived from some source other than sea water, or that sodium is removed from solution by precipitation or adsorption. The latter alternative would appear the more probable.

These sodium analyses are too scanty to allow of any very far-reaching conclusions to be drawn, but it would appear that in most Irish fresh waters the sodium content is likely to be between 0.1 mM. and 0.8 mM., that it is largely derived from rain-borne sea salt, but that the rain-borne sodium is in some cases supplemented by a significant fraction derived from the rocks. The size of this fraction varies presumably with the sodium content of the rock and its rate of weathering.

The lower limit of both sodium and chloride concentrations is, therefore, determined by climatic and geographical conditions alone at a figure of about 0.1 mM., rather less than one five-thousandth of the concentration in which they occur in sea water. This dilution, great as it is, is not too great for the absorptive powers of the majority of fresh-water animals. Krogh (1939, p. 202) described a lake in central Sweden in which the concentration of chloride averages less than 0.07 mM., but which contains quite an extensive and varied fauna in which all the principal fresh-water groups are represented. It may be that some species find a concentration of 0.1 mM. uncomfortably low, at any rate for sodium (for the absorption of sodium

and chloride ions does not necessarily proceed *pari passu*), and are for this reason excluded from waters in eastern Ireland that flow off sodium-poor rocks. But such waters are likely to be of a generally oligotrophic type—poor in potassium, phosphates, and nitrates, as well as sodium, and it would be very difficult to separate the influence of these factors. In general, the supply of sodium chloride in any Irish fresh water is probably sufficient for all those animals for which it is in other respects suited as a medium.

Calcium Content.

A few calcium analyses have been made. The higher values recorded are of little interest: hard waters may have anything from 1 mM. to about 15 mM. Ca per litre, and the variation within this range indicates chiefly how far water that has become saturated with calcium carbonate has been diluted. Waters with less than 1 mM. Ca per litre are usually reckoned as soft, and here it is of some interest to inquire into the lower limit of the calcium content, and into the source from which this calcium is derived. The figures for some very soft waters are given below.

	Ca (mM.)
L. Acorrymore (Achill I.)	0.10
Doolough, Co. Mayo	0.038
L. Muskry (Galtee Mts.)	0.19
Bog-pool, Recess, Co. Galway	0.085
L. Craiggamore, Co. Galway	0.155
L. Nahanagan, Co. Wicklow	0.038

The lower limit of calcium concentration appears to be at about 0.03 mM. (rather more than 1 part per million). Small though this figure is, it represents from five to ten times the amount of rain-borne calcium, calculated from the chloride content of the water and the Ca/Cl ratio of sea water. Nearly all the calcium, therefore, even in these very soft waters, must be derived from weathering of rock or from blown dust or sand. Blown dust is an important factor in the mineral balance of base-poor soils in some parts of the world (*e.g.* the Alps), but it is difficult to imagine that in the wet climate of Ireland it plays a very important part. On the other hand, in a lake such as L. Acorrymore, which lies entirely in a quartzite basin, it is difficult to ascribe any measurable quantity of calcium to weathering of the rock.

For animals with calcareous shells or exoskeletons the calcium content of the water is, of course, of great importance, and concentrations of less than about 0.15 mM. are probably inadequate for proper deposition of calcium carbonate in many such species. But the question of acidity is also relevant here, and although all acid waters are soft we have seen above that some very soft waters are almost neutral. Further faunistic and chemical data are required before we can say whether acidity or lack of calcium is the factor which excludes certain molluscs and crustacea from most mountain waters.

Summary.

A common source of error in the colorimetric determination of *p*H in badly buffered waters is discussed, and a method of eliminating it is described.

The *p*H of Irish fresh waters varies from 4.1 to 8.75. Values above 7.5 are found only in waters running off limestone or basalt; these have mostly a *p*H between 8.25 and 8.5. Only those waters that drain off substantial peat-bogs are strongly acid. The *p*H of such waters is 4.1–4.2 in the Wicklow Mts., 4.3–4.5 in Connemara, and 4.5–5.1 in Kerry. A very large number of mountain lakes and streams that are usually supposed to be strongly acid are, in fact, nearly neutral (*p*H 6.2–7.3). Such waters contain very little acid or base, and are consequently very badly buffered. Their slight acidity is due to carbon dioxide. Such neutral lakes may be surrounded by acid bogs; in such cases the acid that drains into the lake must be precipitated or destroyed; it is not neutralized.

In most waters the variation of *p*H with weather and season is comparatively slight.

The titratable acidity of Irish waters ranges from 0 to 0.47 mEq. per l., for a sample with *p*H 4.1. This indicates that fairly strong acids are present. Titration curves show no sharp inflexion. The titratable alkalinity (excess base) may be as high as 3.6 mEq. per l., and probably higher.

The concentration of chloride is from 0.12 to 0.86 mM. (4.3 to 30.6 parts per million). It is probably all derived from rain-borne sea spray. The highest concentrations are found near the west coast, the lowest in the east. The figures for sodium (0.13 to 0.68 mM.) show a fairly close correlation with those for chloride, suggesting that most of the sodium is also rain-borne, but in some waters a significant fraction seems to be of terrestrial origin.

The calcium concentration in the softest waters may be as low as 0.038 mM. (1.5 parts per million).

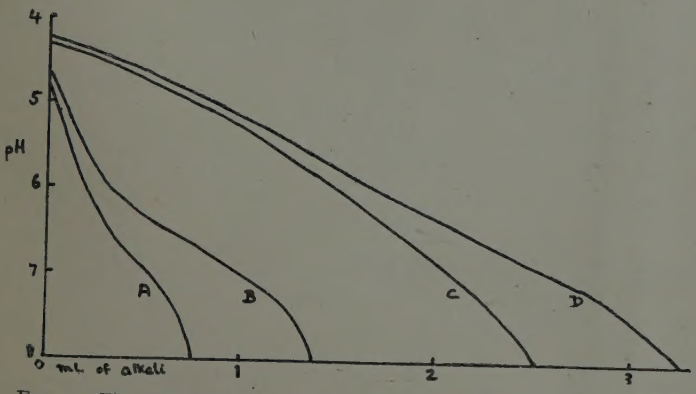

FIG. 1. Titration curves, against N/200 alkali, of 50 ml. samples of:—A, Water from L. Bray, boiled to expel CO_2. B, the same, unboiled, C, water from a bog-pool on the Two-Rock Mountain, boiled to expel CO_2. D, the same unboiled.

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